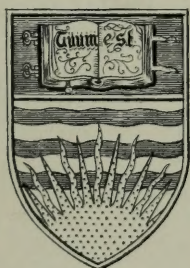


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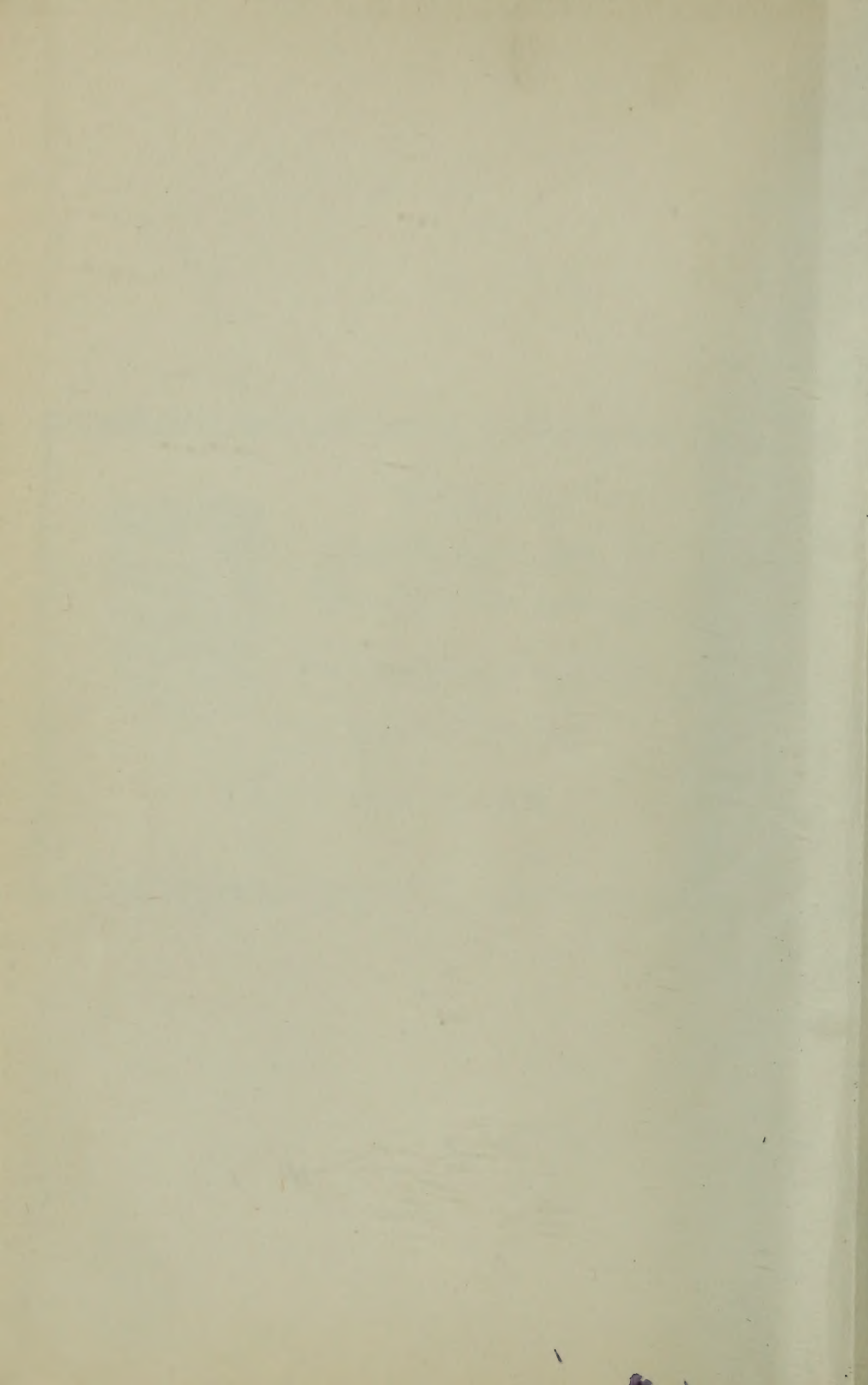
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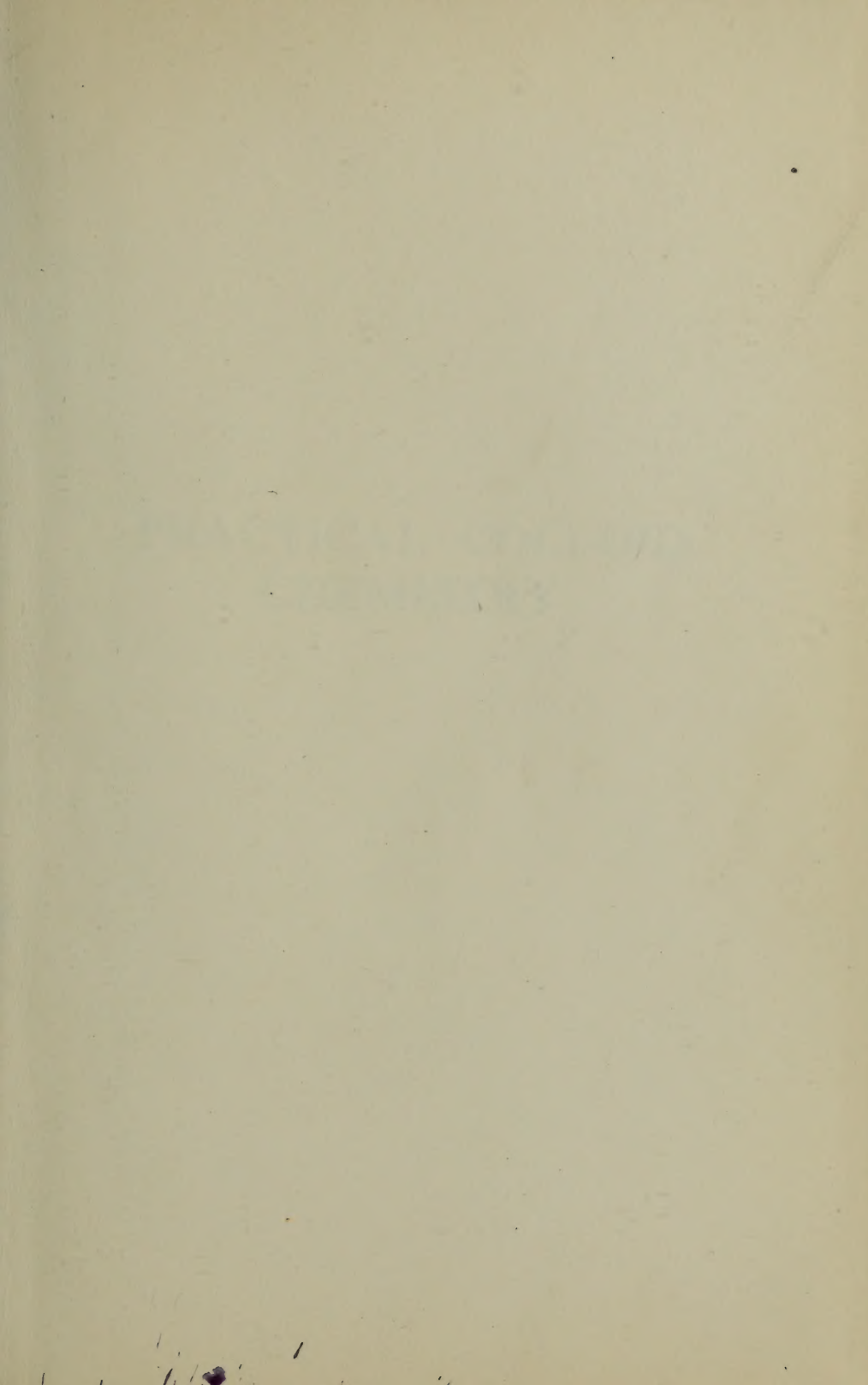


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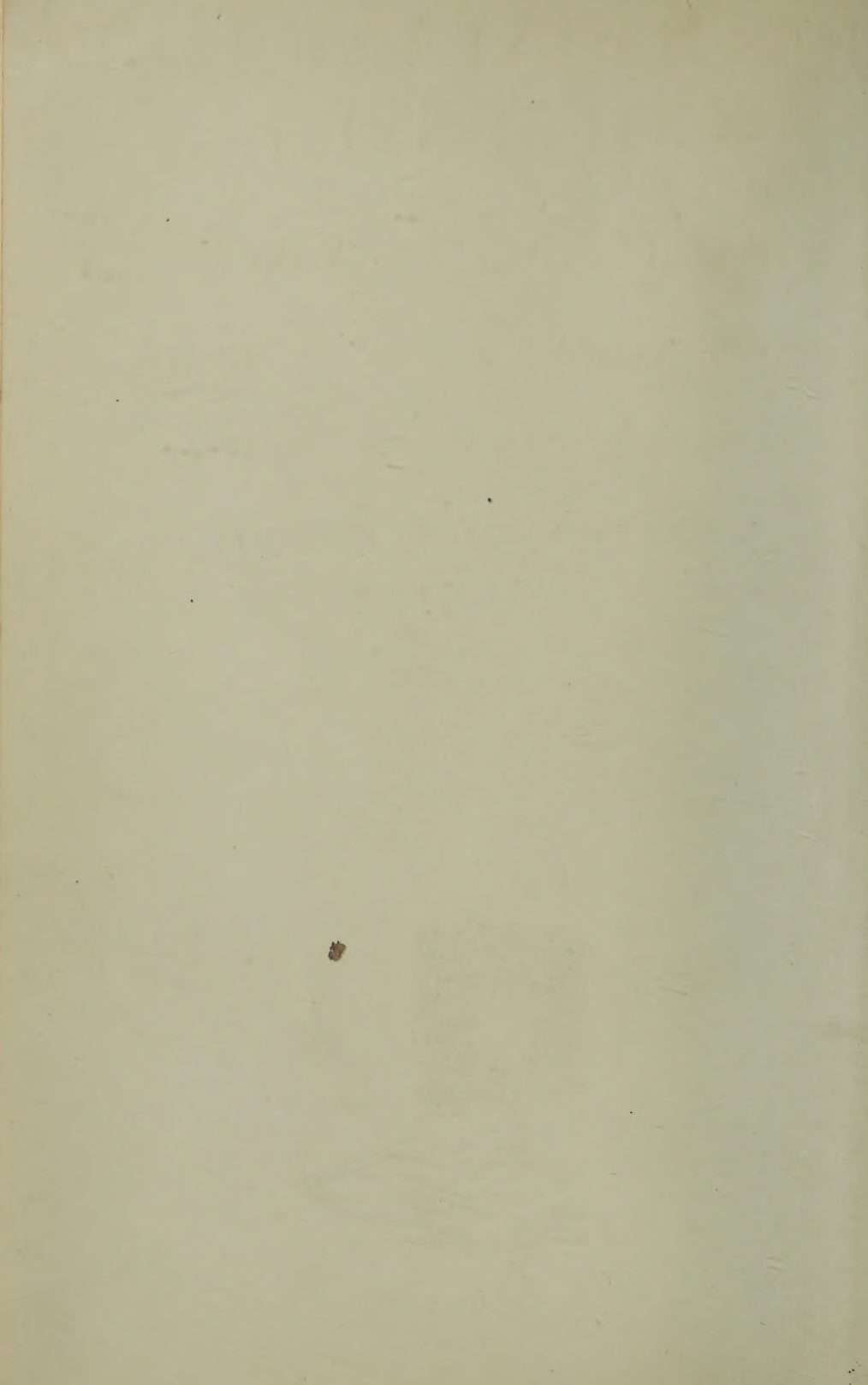
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**PRACTICAL COLLOID
CHEMISTRY**



PRACTICAL COLLOID CHEMISTRY

BY

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WITH 22 ILLUSTRATIONS



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PREFACE TO FOURTH EDITION

THIS book has been received so favourably that three editions were exhausted within two years. The author attributes this to the dire need for experimental knowledge of colloid chemistry after a period of theoretical interest in this science. If this be the explanation, it is all the more gratifying that this manual of experimental colloid chemistry has been welcomed to such an extent.

The rapid sequence of the previous editions made it impossible to keep abreast of advances in colloid chemistry. Therefore, the present edition has been revised and re-edited in many respects. The experiments in this manual were performed and the procedures tested many times during the last four or five semesters by about two hundred students under the supervision of the author and Drs. P. Wolski and A. Kuhn. As a result, previous errors have been corrected and fifteen new experiments have been added, which include Chapter X on elementary dispersoid analysis. The author has also received suggestions from colleagues and invites such in the future.

Some reviewers of the book suggested an index. The author purposely omitted it in previous editions because the manual contains a systematically arranged list of the experiments in the table of contents. If the manual is to give a survey of experimental colloid chemistry, it is preferable that the student learn to recognize systematic

colloid phenomena in conjunction with the experiments. Inspection of the manual readily reveals the chapter in which certain types of experiments are to be found. This manual is, of course, no reference work, but it does give a systematic presentation of the phenomena of colloid chemistry.

WO. OSTWALD

LEIPZIG *May, 1924*

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PRACTICAL COLLOID CHEMISTRY

I

PREPARATION OF COLLOIDAL SOLUTIONS¹

A. CONDENSATION METHODS

CONDENSATION methods for the preparation of colloidal solutions are applicable to molecular disperse systems. Certain molecules of such a solution are brought into the colloid state by coalescence. This is obtained by stabilizing the precipitating particles so that they will remain dispersed within the range of colloid dimensions.

CONDENSATION BY DECREASE IN SOLUBILITY

Expt. 1. Add drop by drop with continuous stirring 5 to 10 c.c. of a 3 per cent. alcoholic solution of mastic or colophony to 100 c.c. of distilled water. The resulting milky white, strongly opalescent sol may be freed from the coarser particles by filtration. The alcohol may be removed by heating the colloidal solution which inci-

¹ An excellent presentation of the methods of preparation is given by The Svedberg, *Preparation of Colloidal Solutions of Inorganic Substances*, 3rd edition, Dresden, 1922.

dentally produces a partial coagulation of the sol. Unheated sols remain stable for years.

A **paraffin hydrosol** may be prepared in a similar way from a dilute alcohol solution of solid or liquid paraffin, i.e. a 2-3 per cent. solution, otherwise most of the particles are coarsely disperse.

A **selenium sol** (A. Gutbier) is obtained by dissolving precipitated selenium in concentrated hydrazine hydrate and pouring a few drops of this solution into distilled water. The resulting sol is red and opalescent.

A **sulphur sol** (P. P. von Weimarn and B. Malytschew) is prepared by adding a saturated solution of sulphur in absolute alcohol to a large volume of distilled water.

Colloidal emulsions as castor oil, petroleum, essential oils such as oil of rosemary and cassia are all similarly prepared by precipitation from dilute alcohol solutions.

CONDENSATION BY CHEMICAL PRECIPITATION

Colloidal gold—One per cent aqueous solutions of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ or AuCl_3 are used throughout these experiments. Each solution is made neutral or very slightly alkaline to litmus by cautious addition of pure Na_2CO_3 . Excess of hydroxions as well as impure carbonate decompose the solution. If the solution is to be preserved for further use, neutralize and dilute 100 times (0.01 per cent.) the desired amount of the 1 per cent solution previous to performing the experiment.

Expt. 2. **Red gold sol prepared with tannin**—Heat to boiling 100 c.c. of distilled water and 5-10 c.c. of the 0.01 per cent. gold solution in an Erlenmeyer flask. To this solution add, drop by drop, a freshly prepared 1 per cent. aqueous tannin solution. Stir intermittently for 30 seconds and continue adding the tannin solution until an intense red coloration is obtained. Appreciable

amounts of gold chloride and tannin may be added before coarsely disperse blue or grey green metallic depositions form. Only fresh tannin solutions must be used because old solutions spoil despite the addition of preservatives.

This experiment is especially suited for demonstration, because the sol is usually non-sensitive to the impurities of distilled water in the presence of tannin. Gold may be preserved for years with chloroform and toluol without any more than a slight browning. A sensitive sol may, however, be prepared by avoiding an excess of tannin (J. Matula). Such a sol is used to demonstrate the phenomenon of colour transition from red to blue as will be described below.

Expt. 3. Red gold sol prepared with alcohol—Heat to boiling 100 c.c. of distilled water and 5 to 10 c.c. of 0.01 per cent. gold solution. Remove the burner, and add proportionately 5 to 10 c.c. of concentrated alcohol with constant stirring. Continue heating for 15 to 20 minutes until the distinct cherry-red colour appears. More gold solution and alcohol may be added to this sol without any marked change in its red coloration. The characteristic red colour of the sol persists even on strong evaporation, but is immediately transformed to blue violet upon addition of electrolytes. This gold sol is strongly sensitive to electrolytes in marked contrast to the tannin gold sol.¹

Expt. 4. Blue gold sol prepared with hydrazine hydrate (A. Gutbier)—To a mixture of 100 c.c. of water and about 10 c.c. of a 0.01 per cent. unneutralized gold solution, add a few drops of a diluted hydrazine hydrate

¹ On the preparation of red gold sols with formaldehyde, see R. Zsigmondy, *Liebigs Ann.*, 301, 30 (1898); *Z. phys. Chem.*, 56, 65 (1906); H. Morawitz, *Kolloidchem. Beihefte*, 1, 324 (1910); The Svedberg, *loc. cit.*

solution (1 c.c. of the C.P. 50 per cent. solution diluted with a litre of water).

Phenylhydrazinechlorhydrate and hydroxylaminehydrochloride may be used in the same concentration to replace hydrazinehydrate.

Expt. 5. Gold sol prepared with illuminating gas—Gold sols may be obtained by the continuous passage of coal gas for about 24 hours into 100 c.c. of 0.01 per cent. neutralized gold solution. The colours of the sols, red, violet or blue, depend upon the carbon monoxide concentration of the illuminating gas. Carbon monoxide, prepared by heating oxalic and sulphuric acids and washing the gas, yields sols of a distinct red coloration especially if distilled water or conductivity water has been used (J. Donau).

Expt. 6. Green gold sol prepared with alcohol—Follow the procedure in Expt. 3 and use concentrated gold solutions; 100 c.c. of a 0.01 per cent. solution and 5 to 10 c.c. of alcohol. The blue-green sols obtained are coarsely disperse and unstable.

Expt. 7. Gold sols prepared with combustion gases—Direct a hydrogen flame (J. Donau) or more simply a small Bunsen flame¹ obliquely across the surface of a gold solution (10 to 20 c.c. of 0.01 per cent. gold solution and 100 c.c. of water) contained in a porcelain dish. Stir the solution continuously by means of a glass rod. A red to a red-violet sol is obtained after 5 to 10 minutes. Further reduction is obtained by holding the burner at a distance and is manifested by a deepening of the colour.

Expt. 8. Gold sol prepared with a solid dispersion medium (J. Donau)—Heat some borax contained in a platinum loop, dip it into a 0.01 per cent. (or more diluted)

¹ A very luminous Bunsen flame will contaminate the solution with soot particles.

gold solution and heat again until the formation of a clear molten mass. Beads are obtained whose colours depend upon the quantity of gold and the duration of heating. Some of the beads are ruby-red and transparent, while others appear dark blue in transmitted light and yellow-brown in reflected light.

Coloured sols are also obtained by fusing microcosmic salt with gold chloride in a porcelain crucible and then pouring the molten liquor drop by drop upon a glass plate. With increasing amounts of gold chloride one obtains pearls that appear ruby-red to yellow in reflected light and blue in transmitted light.

COLLOIDAL SILVER

Expt. 9. **Silver sol prepared with tannin**—Add a few drops each of freshly prepared 1 per cent. tannin solution and 10 per cent. sodium carbonate solution to about 100 c.c. of a 0.001N solution of AgNO_3 . Upon warming, an intense red to yellow-brown sol is obtained, which is not very sensitive to electrolytes.

Expt. 10. **Silver sol prepared with hydrazine hydrate** (A. Gutbier)—Add a few drops of the diluted hydrazine hydrate solution (1 c.c. of C.P. 50 per cent. solution diluted in a litre of water) to 100 c.c. of a solution containing 1 c.c. of 0.1N AgNO_3 in a litre of water. Upon heating, a sol is obtained which is bright yellow in transmitted light and green in reflected light. Silver sols of other colours may be prepared according to Expt. 94.

COLLOIDAL SULPHUR (M. RAFFO)

Expt. 11. Dissolve 50 g. of crystalline sodium thio-sulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 30 c.c. of water. Weigh 70 g. of concentrated H_2SO_4 in a 300 c.c. beaker and keep

on ice. Add the thiosulphate solution, drop by drop, preferably from a dropping funnel into the sulphuric acid. This yields a thick yellow mass. Add further 30 to 50 c.c. of water, warm on the water-bath for 10 to 15 minutes to drive off the formed SO_2 . The mass now becomes a clear yellow liquid. After cooling, filter over glass wool or through a coarse towel, yielding a concentrated colloidal milk of sulphur contaminated with Na_2SO_4 . The sol becomes clear on warming and again cloudy on cooling. Such sols containing very small amounts of sulphate may be kept for a long time without any appreciable decomposition. Purification of the sol by dialysis is possible to only a limited extent, since small quantities of Na_2SO_4 are indispensable for its stability.

A sulphur sol can be prepared more simply by neutralizing with hydrochloric acid a very dilute solution of ammonium sulphide, yielding a distinctly opalescent solution.

Sulphur sols of different degrees of dispersion may be prepared according to the method of S. Odén [*Koll. Zeitschr.* 8, 196 (1911); 9, 100 (1911)].

COLLOIDAL SULPHIDES

Expt. 12. **Arsenic trisulphide hydrosol** (H. Schulze)—Prepare a saturated solution of arsenious acid by boiling As_2O_3 in water. Upon cooling to room temperature the strength of the solution is about 2 per cent. Dilute 50 c.c. of this solution to 200 c.c. to give a 0.5 per cent. solution. Pass in a stream of H_2S for about five minutes. An intense yellow to yellow-red sol is obtained which turns green-yellow on dilution. Concentrated sols may be prepared by further addition of the arsenious acid to the already prepared sol and may

again be precipitated from it. Coarsely disperse aggregates that may form should be filtered or separated by dialysis.

Expt. 13. **Antimony trisulphide hydrosol** (H. Schulze)—An intense yellow-red sol is obtained directly by bubbling H_2S into a solution of 0.2 to 0.3 g. of tartar emetic (potassium antimonyl tartrate). The H_2S must not be passed in for too long a time else slight coalescence results. The sol may be purified by dialysis.

Expt. 14: **Mercuric sulphide hydrosol** (A. Lottermoser)—Pass H_2S into a saturated solution of $Hg(CN)_2$ or into a diluted solution (a few drops of the concentrated to 200 c.c. of water). A deep brown sol is obtained without any aggregates.

Expt. 15. **Mercuric sulphide alcosol** (A. Lottermoser)—Pass H_2S into a saturated solution of $Hg(CN)_2$ in 97 per cent. alcohol and a dark brown alcosol results which, on inspection, appears like the hydrosol.

HALIDE AND CYANIDE HYDROSOLS

Expt. 16. **Silver iodide hydrosol** (A. Lottermoser)—Add 2 c.c. of 0.1N $AgNO_3$ to a dilute KI solution (2 to 3 c.c. 0.1N KI in 100 c.c. of water) and a green-yellow milky sol results. Most of the KI may be removed by dialysis, although the sol is quite stable for months without any dialysis.

Concentrated but less stable sols may be prepared by adding 7 to 8 c.c. of 0.1N $AgNO_3$ to 20 c.c. of 0.05N KI, or by adding 5 to 6 c.c. of 0.1N KI to about 20 c.c. of 0.05N $AgNO_3$. The first sol is more stable than the second. The proportions as given are essential for making good sols. See A. Lottermoser, *Zeitschr. f. physik. Chemie* 62, 370 (1908); *Journ. f. prakt. Chemie* 73, 374 (1906). The electrical charges of these sols are as given in Experiment 101.

Expt. 17. **Silver chloride and bromide hydrosols**—Add about 2 to 3 c.c. of 0.1N solution of KCl or KBr to 100 c.c. of water with stirring and then add 1 to 2 c.c. of 0.1N AgNO_3 . A milk-white silver chloride sol and a grey silver bromide hydrosol result. Cf. Expt. 44 for the stability of these sols.

Expt. 18. **Prussian blue hydrosol**—Add a freshly prepared, diluted solution of FeCl_3 (without warming) to a diluted solution of potassium ferrocyanide (0.1 gr. per litre). The amount of FeCl_3 added must be less than that required by the molecular proportion, $\text{FeCl}_3 : \text{K}_4\text{Fe}(\text{CN})_6 = 1 : 2.3$.

Concentrated stable hydrosols may be prepared by mixing concentrated solutions of FeCl_3 and potassium ferrocyanide. The ferric chloride solution is added drop by drop with constant stirring until a thick paste results. Sols of any concentration are obtained by adding the paste to water.

Expt. 19. **Copper ferrocyanide hydrosol**—Add 1 per cent. CaSO_4 or CaCl_2 to 100 c.c. of the dilute $\text{K}_4\text{Fe}(\text{CN})_6$ used in Expt. 18. A clear brown-red stable sol is obtained.

HYDROXIDE AND OXIDE HYDROSOLS

Expt. 20. **Ferric hydroxide sol** (Krecke)—Heat to boiling about 200 c.c. of distilled water. Add about 20 c.c. of freshly prepared, yellow 2 per cent. FeCl_3 solution and an intense red-brown sol is obtained after a few minutes. Since this hydrosol is reversible on cooling, it is best to dialyse it while warm.

Expt. 21. **Ferric hydroxide sol by hot dialysis**—Prepare a collodion dialysing sac according to Expt. 54. Suspend it in a beaker of water and fill the sac with 0.01 M. FeCl_3 . Place the arrangement on a water-

bath. Change the water contained in the beaker until the test for chloride is negative. Quantities of hydrosol up to 50 c.c. are dialysed completely within two days provided the arrangement is kept in a warm place overnight. Salt solutions of concentration greater than 0.01 M. coalesce.

Expt. 22. **Ferric hydroxide sol** (Thomas Graham)—To a half saturated solution of FeCl_3 add gradually a 2N $(\text{NH}_4)_2\text{CO}_3$ solution until the resulting precipitate continues to dissolve on stirring. Dialyse preferably by warming.

See Expts. 36 and 102 for the dispersion method of preparing concentrated $\text{Fe}(\text{OH})_3$ sols.

Expt. 23. **Aluminium hydroxide sol**—Dilute a 10 per cent. solution of aluminium acetate twenty times and warm on a water-bath until the odour of acetic acid disappears. The resulting $\text{Al}(\text{OH})_3$ sol is clear and colourless. The sol is easily detected and its concentration determined by precipitating it with aqueous $\text{K}_4\text{Fe}(\text{CN})_6$.

See Expts. 32 and 37 for dispersion methods of preparing concentrated sols.

Expt. 24. **Manganese peroxide sol** (J. Cuy)—Warm a 0.05N solution of KMnO_4 to boiling and add gradually concentrated NH_4OH until the solution is coffee coloured. Boil until the last traces of ammonia have been expelled. The KOH formed in the reaction does not interfere with the sol and need not be neutralized. The sol is clear, transparent, brown and stable when unexposed to air. It is easily coalesced by contact with filter or parchment paper. Sols incompletely reduced to MnO_2 are unstable. They appear red due to the presence of undecomposed KMnO_4 and coalesce upon filtration. The supernatant liquid is also red. Addition of alcohol colours it yellow due to reduction of KMnO_4 . The sol

may be maintained stable by addition of small amounts of alcohol.

Expt. 25. **Silicic acid sol and gel**—Add a 5 per cent. solution of water glass¹ to 100 c.c. of 0.1N HCl and stir. The resulting sol must be acid to avoid spontaneous gelation.² If acid, the solution will be colourless to phenolphthalein. Colloidal SiO₂ is detected by precipitation with ammoniacal cupric oxide or Ba(OH)₂.

Silicic acid gel is prepared by adding a 10 per cent. water glass solution to an equal volume of 2N HCl. The gel first appears clear and then opalescent.

COLLOIDAL ALKALI AND ALKALI EARTH SALTS

Expt. 26. **Sodium chloride sol in benzol** (C. Paal)—Sodium malonic ester and ethyl chloracetate react on warming to form NaCl and ethyl ethylene tricarboxylate. Prepare a benzene solution of sodium malonic ester as follows: Add 5 g. of malonic ester (CH₂[CO₂C₂H₅]₂) to 30 g. of benzol (previously dried over sodium) and then add 0.7 g. of sodium wire. Transfer the solution to a flask fitted with a reflux condenser and warm on a water-bath until the sodium is completely dissolved. Allow the solution to cool, add 4.0 g. of chloracetic acid ester (ClCH₂CO₂C₂H₅) and again warm with continuous stirring. With dry benzene the resulting sol is usually yellow and strongly opalescent.³ The yellow, highly

¹ The concentration of commercial water glass varies considerably. The Merck pharmaceutical preparation is a 10 per cent. solution. The concentrations of sodium silicate solutions referred to in the text are based on ash determinations.

² A preliminary experiment is advisable in order to determine how many c.c. of water glass are necessary for instantaneous solidification and one-third to one-half of this amount is used in the experiment (R. Zsigmondy).

³ At times an opalescent rigid gel is formed.

disperse sol becomes white and coarse with evident sedimentation when the benzene used contains water or when the sol is allowed to stand. The yellow sol may be kept stable for years in a well-stoppered container.¹

Expt. 27. **Sodium chloride gel** (L. Karczag)—Dry carefully 15 to 20 g. of sodium salicylate in order that the gel to be prepared may be obtained without difficulty. Pour 20 g. of thionyl chloride (SOCl_2) into a glass-stoppered vessel under a hood and add to it 15 to 20 g. of the dried sodium salicylate. The flask is kept loosely stoppered to permit the escape of SO_2 formed in the reaction. After a short time the lower layers of the salicylate appear to be gradually transformed into a green-orange opalescent gel. The process is complete within a day and the resulting gel is of the consistency of soft soap. The gel, kept sealed up, remains stable for several weeks.

Expt. 28. **Calcium carbonate alcosol** (C. Neuberg)—Heat lime (CaO) to glowing, pulverize and add 2 to 3 gr. to 50 c.c. of freshly distilled absolute methyl alcohol. Pass CO_2 into this solution for several hours. The CaO is thereby completely dissolved. Decant the supernatant blue-yellow opalescent organosol of CaCO_3 . The milky sol is transformed into a gel in the presence of excessive CaO and on prolonged standing in the cold. This alcosol remains stable for weeks in sealed containers.

B. DISPERSION METHODS

Dispersion methods for the preparation of colloidal solutions involve the continuous division of non-disperse or coarsely disperse substances into the colloidal state.

¹ The author has a preparation that has remained of a milky consistence since 1910.

COLLOID FORMATION BY MECHANICAL DISPERSION

Expt. 29. A suspension of potato starch in cold distilled water is decomposed by a baryta filter so that no iodine reaction is obtained for the filtrate. On the other hand, some moist starch ground in an agate mortar yields a starch hydrosol, most of which passes through the filter and gives a positive iodine reaction for the filtrate (G. Wegelin).

Starch granules, according to a private communication from H. Luers and C. Lintner, may contain occluded substances which disperse spontaneously on mere standing of starch in water.

CHEMICAL DISPERSION METHODS

Chemical dispersion methods involve the use of freshly prepared precipitates which are transformed into the colloid state. These precipitates usually contain adsorbed electrolytes which have a coagulating effect on colloids and hence retard colloid formation; for example, H_2SO_4 in the precipitation of CdS by bubbling H_2S into CdSO_4 . Electrolytes so formed must be partially washed from the precipitate because an optimum concentration of electrolyte is indispensable in the formation of stable hydrosols. Precipitation ordinarily occludes too great a concentration of "sol-forming ions." Washing with water until optimum ionic concentration of the precipitate is attained yields a stable hydrosol provided that coagulating ions are simultaneously removed (Expts. 30-34). The precipitate may first be washed completely or decanted free from the ions which retard colloid formation and then a definite concentration of electrolyte added to obtain the desired hydrosol. This process is known as peptization (Expts. 35-39).

A. CHEMICAL DISPERSION METHODS BY WASHING

Expt. 30. **Silver chloride hydrosol**—To 20 c.c. of 0.01N AgNO_3 add more than the equivalent amount of 2N NH_4Cl , i.e. about 15 drops and filter. The last portions of the filtrate are clear. Wash the precipitate with water until the filtrate becomes clear. The milky portions obtained consisted of the AgCl hydrosol. This indicates that the optimum ionic concentration has been exceeded. Good results are obtained with the concentration given.

Expt. 31. **Cadmium sulphide hydrosol**—To a 5 to 10 per cent. solution of CdSO_4 add concentrated NH_4OH until the resulting precipitate continues to dissolve. Pass in H_2S for about 5 minutes. A heavy precipitate and a yellow coloured supernatant liquid results on standing. Wash by decantation until the precipitate settles more slowly; if the solution is now filtered, the filtrate will be found to consist of a concentrated hydrosol.

Expt. 32. **Aluminium hydroxide sol**—The ionic concentration necessary for sol formation is attained by evaporation (W. Crum, J. Gann). Dilute a concentrated solution of commercial aluminium acetate to twice its volume with concentrated acetic acid and heat on a water-bath. A granular white precipitate forms in several minutes. Decant the supernatant liquid and repeatedly wash the precipitate with distilled water; centrifuge and repeat the washing. The precipitate is thereby gradually dissolved forming the desired suspension. If this turbid suspension is heated, it forms a perfectly clear sol. A very concentrated suspension forms only turbid solutions. The dilute sols may be concentrated by evaporation without becoming turbid. Heat the sols on a water-bath for a day to remove the excess of acetic acid. Replace the water lost by evaporation.

For another, more rapid method of preparation, see Expt. 37.

Expt. 33. **Vanadium pentoxide sol** (W. Biltz)—Triturate in a mortar about 5 g. of ammonium vanadate with a few drops of hydrochloric acid. Filter the red precipitate and wash it continuously until the filtrate assumes a dark red colour. The precipitate is thus peptized. Wash it into an Erlenmeyer flask, add about 200 c.c. of water and stir. Within a few hours a dark red solution is obtained which is fairly clear to transmitted light.

Expt. 34. **Congo-rubin blue hydrosol** formation and dissolution of a sol with variation in hydrion concentration. Add HCl to 20 c.c. of a 0.1 per cent. solution of Congo rubin, until precipitation is complete. Allow the mixture to stand about 24 hours for complete settling of the precipitate. Decant the supernatant liquid and distribute the precipitate between two hard filters. The filtrate should be colourless and without any blue tinge. If not, wash the precipitate with some dilute 2N HCl. Finally wash the precipitate on both filters with distilled water. Since the precipitate adheres to the filter paper, the washings may be hastened by decantation. Continue to wash until an intense dark blue hydrosol passes through the filter.¹

When both precipitates are in the stage of hydrosol formation, add dilute HCl to one filter and water to the other. Hydrosol formation ceases very quickly in the acidified filtrate which becomes colourless. The non-acidified precipitate is in a state of sol formation while the other is prevented from sol formation by the excessive hydrion concentration. These states are reversible for the same precipitate any number of times by changing

¹ Usually the filtrate shows a violet coloration previous to actual hydrosol formation.

the hydron concentration. The precipitate which yielded a blue filtrate with water will give a colourless filtrate with dilute HCl. Conversely, the precipitate which yielded a colourless filtrate with HCl will give a blue filtrate with water.

For class demonstration use two porcelain suction filters and a water suction pump.

B. CHEMICAL DISPERSION BY PEPTIZATION

Expt. 35. Mercury sulphide hydrosol by washing and peptizing—Pass H_2S into 20 c.c. of saturated mercuric chloride solution until the greyish-white precipitate first formed, turns black. Filter or decant the supernatant liquid and wash repeatedly with distilled water. Suspend a portion of the precipitate in water and again treat with H_2S for about ten minutes. Most of the precipitate is thus obtained in colloidal solution.

Expt. 36. Ferric hydroxide sol ; peptization by the addition of sol-forming ions. Add a sufficient amount of ammonium hydroxide, drop by drop, to a ferric chloride solution (5 c.c. of saturated $FeCl_3$ solution in 100 c.c. of water) until the supernatant liquid is tinged red. Wash the precipitate several times by decantation and transfer it to an Erlenmeyer flask. Add about 40 c.c. of H_2O and shake until a thick consistency is obtained. Pour 5 c.c. of this solution and then about 100 c.c. of distilled water into each of five Erlenmeyer flasks. Retain flask 1 for a control. Add a few drops of 0.1N HCl to flasks 2 and 3, and a few drops of the original $FeCl_3$ solution to flasks 4 and 5. Shake the flasks vigorously. After 10 minutes the colourless supernatant liquid in each flask appears brownish red due to hydrosol formation. Complete dissolution of the precipitate may be obtained by

adding calculated amounts of HCl or FeCl_3 . On standing, the hydrosol becomes intensely red.

Compare this with Experiment 102 on the negative ferric hydroxide sol.

Expt. 37. Aluminium hydroxide sol by peptization with HCl—Precipitate the hydroxide from a dilute 0.01N solution of AlCl_3 or $\text{Al}_2(\text{SO}_4)_3$ with ammonium hydroxide. Allow the precipitate to settle or centrifuge it. Decant and wash the precipitate several times with distilled water. By addition of a few drops of dilute HCl, dilution and long heating, the precipitate again forms an opalescent suspension which passes through a baryta filter. The sol is more coarsely dispersed than those in Expts. 23 and 32, which gave practically clear hydrosols.

Expt. 38. Prussian blue by peptization with oxalic acid—Add about 5 c.c. of saturated aqueous $\text{K}_4\text{Fe}(\text{CN})_6$ to 10 c.c. of 0.05 m. FeCl_3 , filter and wash the precipitate. Pour several portions of 0.1N oxalic acid over the precipitate. The resulting filtrate constitutes the desired blue coloured sol.

Expt. 39. Stannic acid hydrosol by peptization with ammonium hydroxide—Prepare a dilute solution of stannous chloride by dissolving 1 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 300 c.c. of H_2O . Pour this solution into a filter flask fitted with a stopper and a long glass tube. Draw air through the solution for about two days by means of a suction pump. The turbid solution becomes clear and then turbid again. Continue to draw air through the solution until a precipitate forms. Decant and wash (R. Zsigmondy). This procedure requires several days if dilute solutions are used. To hasten the process, warm the solution as soon as it has become turbid by aeration in order to obtain the coarse flocculent precipitate. Decant and filter the supernatant liquid.

Wash the precipitate with hot water until the washings give no test for chlorides. Add a few drops of dilute ammonium hydroxide, warm until the precipitate dissolves to form a clear solution of stannic acid hydrosol. Heat to drive off excess ammonia.

The sol is obtained more quickly if anhydrous stannic chloride is used. Add, drop by drop, a solution of stannic chloride to a relatively large volume of water. Wash the precipitate and add ammonium hydroxide as above to obtain the desired sol. The sol may be prepared very conveniently by using the hydrate, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Add, drop by drop, a 5 per cent. solution of this salt to boiling water. Compare this with the preparation of colloidal ferric hydroxide in Expt. 20. The thick flocculent precipitate forms immediately and gives a hydrosol when treated as above. This procedure takes less than an hour if the washing is hastened by the use of a porcelain funnel and suction pump.

The sol may be coalesced by the addition of neutral salts, caustic alkalies or dilute acids. A typical property of these sols is the ease with which they foam.

To prepare stannic acid hydrosols of different degrees of dispersion, see M. Mecklenburg, *Zeitschr. f. anorg. Chem.*, 74, 207 (1912).

ELECTROLYTIC METHODS OF DISPERSION

Expt. 40. **Preparation of colloidal metals and metallic oxides by electrical dispersion**—This method consists in the disintegration of wire electrodes by producing an electric arc between the ends. Insert two silver wires 0.5–1 mm. in diameter in narrow glass or rubber tubes for insulation. Connect the wires with a 110 volt direct current and introduce a variable resistance in the circuit. The current flow should be 4 to 12

amperes. Place the two electrodes about 2 or 3 mm. apart in a porcelain dish or glass beaker containing water and ice. One or both electrodes may be held to a small support. Regulate the current so that a green coloured arc forms between the ends of the electrodes when they are brought near one another. Dark brown or olive-green clouds of dispersed metallic and oxidized silver form in the water. Colloid formation is favoured by adding a few drops of 2 per cent. Na_2CO_3 solution to the water. Silver and platinum disintegrate very readily, gold with difficulty.

Expt. 41. **Preparation of colloidal lead by electrolysis** (G. Bredig and F. Haber)—A lead plate, fitted with a binding post, is used for the anode. A lead wire, 1–2 mm. diameter, is suspended on a support a short distance from the plate, for the cathode. Immerse both electrodes in a 1 per cent. solution of NaOH contained in a beaker. Pass a direct current of 220 volts through the system. The lead wire disintegrates to form black clouds of lead particles, partly colloidal. Oxidation and flocculation of the dispersed lead particles removes them from the colloid state.

Expt. 42. **Lead pyrosol** (R. Lorenz)—Fuse some well-dried lead chloride. Throw some shavings of pure sheet lead into the melt and observe: first, the lead particles become surrounded with a crust of solid lead chloride and fall to the bottom of the tube; second, the salt melts and the lead particles coalesce into a molten drop similar to that of mercury. At the same time, dark brown clouds of highly dispersed lead begin to form.

It is not known whether the sol formation is due to a condensation of a molecular dispersed vapour or a colloidal solution of lead in the melt.

EXPERIMENTS ON THE THEORY OF FORMATION
OF COLLOIDAL SOLUTIONS

Von Weimarn's rule states that the size of precipitated particles is greatest when medium concentrations of the two reacting solutions are used. With very low or very high concentrations the precipitated particles are smaller.

Expt. 43. Prepare saturated solutions of FeCl_3 and $\text{K}_4\text{Fe}(\text{CN})_6$. Mix the two solutions in the following concentrations :

(a) Add 1 c.c. of $\text{K}_4\text{Fe}(\text{CN})_6$ and 2-4 drops of FeCl_3 to 200 c.c. of H_2O . A very clear permanent sol forms.

(b) Add 1.5 c.c. of $\text{K}_4\text{Fe}(\text{CN})_6$ and 1 c.c. of FeCl_3 to 200 c.c. of H_2O . A voluminous precipitate settles in about half an hour from the deeply coloured solution and the bright blue supernatant liquid becomes almost colourless on standing.

(c) Pour 10 c.c. of the saturated ferro-cyanide solution in a small beaker ; stir and add 2 c.c. of saturated FeCl_3 solution drop by drop. A paste forms which is so viscous and adherent to the beaker that none is lost on inverting it. Take a small amount of this precipitate on a glass rod and put it in about 200 c.c. of water. A clear permanent hydrosol forms.

STABILITY AND MOLECULAR SOLUBILITY OF A
COLLOIDAL SYSTEM

The greater the molar solubility of a precipitate, the less stable it is when in the colloidal state. Since the larger particles grow at the expense of the smaller, a precipitate with a larger molar solubility will change from a finer into a coarser form. In analytical chemistry, a precipitate, which is difficult to filter, is brought to a coarser state by increasing the solubility and thereby

hastening the growth of the particles, by heating for a certain length of time. On the other hand, under similar conditions, the precipitate may occur in a colloidal form when the molar solubility is comparatively small.

Expt. 44. **Solubility of silver halides at 20° C.**

AgCl: 0.0016 g. per litre

AgBr: 0.000084 g. per litre

AgI: 0.0000028 g. per litre

—Dilute 5 c.c. each of tenth-normal solutions of KBr and KI with 100 c.c. of H₂O. Add 3 c.c. of 0.1N AgNO₃ to each of the three solutions with continuous shaking. The precipitates form sols consisting of relatively coarse particles, which coagulate after 1–2 days. The less the solubility of the precipitate, the more rapid the settling.

COLLOID FORMATION IN THE PRESENCE OF PROTECTIVE COLLOIDS

Highly disperse and reversible colloids are stabilized by preparing the colloid in the presence of especially hydrated emulsoids such as gelatin, egg white, tannin, dextrin, etc. A reversible colloid is one which becomes solid upon evaporation and is spontaneously soluble when water is added again. A well-known technical example is the preparation of collargol. The following experiments show the influence of a protective colloid upon the formation of a highly disperse colloid.

Expt. 45. Add 2 drops of 0.1N AgNO₃ to 20 c.c. of H₂O acidified with 4 drops of HNO₃ and divide the solution into two equal portions. Add to the first portion 1 c.c. of a 0.5 per cent. solution of gelatin and to the second, 1 c.c. of water and shake. Add 3 drops of 0.1N HCl to both solutions and shake again. The second solution

becomes white and turbid while the first remains clear.¹ A faint opalescence appears in the first solution after several minutes. This increases after a few hours, but no precipitate forms as in the second.

Expt. 46. Add 5 c.c. of a saturated PbCl_2 solution to 100 c.c. of water. Divide the mixture between two Erlenmeyer flasks. Add 3 c.c. of a 1 per cent. freshly prepared gelatin solution to one flask and pass H_2S into both mixtures for a few minutes. The solution without the gelatin gives a flocculent precipitate, while the other forms a permanent dark brown lead sulphide hydrosol. A thin layer of this solution appears perfectly clear.

Expt. 47. **Preparation of photochloride sols**—Prepare two sols of AgCl according to Expt. 45 and expose both to sunlight or a strong arc light. Sol A gives a beautiful, clear, red-brown, highly disperse photochloride of AgCl and colloidal silver. Sol B gives a turbid, violet-grey coarsely disperse chloride.

¹ Of course the gelatin used must be washed free from chlorides.

II

DIFFUSION, DIALYSIS, ULTRA-FILTRATION

DIFFUSION

COLLOIDAL solutions show little diffusion. Quantitative determinations of the diffusion coefficients are difficult. Dilute jellies of gelatin, agar-agar, or silicic acid influence the speed of diffusion but slightly in semi-quantitative determinations of the rate of diffusion in various disperse systems.

Expt. 48. Prepare a hot 3 per cent. solution of gelatin and pour it half-full into a series of test-tubes. Allow it to solidify at room temperature.¹ Pour various solutions over the jelly. The diffusion of coloured solutions can easily be followed as they penetrate the jelly. Colourless solutions, however, require a reagent previously dissolved in the jelly, as NaCl with diffusing AgNO₃.² An alternative is to heat for a short time and draw out the jelly into long threads. Wash carefully with ice water, cut into long strips and allow the reagent to act upon these strips.

A thin strip of graduated paper pasted over the length of the test-tube will aid in the estimation of the diffusion

¹ In the first case a loosening of the gelatin cylinder from the sides of the tube may occasionally be observed.

² See Expt. 128 on the irregularities which occasionally occur in such diffusion reactions.

coefficient, expressed in millimetres per twenty-four hours.

Determine the diffusion coefficients of the following :—

RATE OF DIFFUSION.	
<i>Practically Zero.</i>	<i>Fairly Rapid.</i>
Black India ink Gold or silver sol Ferric hydroxide sol Mercury sulphide sol Prussian blue Alkali blue Congo red	Methyl violet Acid fuchsine Brilliant green Methylene blue Saturated copper sulphate
<i>Slow.</i>	
Congo rubin	

The determination of the rate of diffusion detects "transition-systems," i.e. substances in a state between truly colloidal and truly molecular. Thus, Congo rubin shows considerable diffusion after 3 or 4 days, while Congo red only 1 to 2 weeks.

Expt. 49. Diffusion analysis of polydisperse systems—Add sufficient dilute alkaline aqueous eosin to a solution of "night blue" until the mixture appears dark violet. The red eosin penetrates the jelly in twenty-four hours, while the "night blue" does not diffuse.

Other colour mixtures suitable for such experiments are :

(a) Alkali blue + picric acid. The yellow dye diffuses out of the green mixture.

(b) Alkali blue + acid fuchsine. The red dye diffuses out of the blue-violet mixture.

Expt. 50. Add silver nitrate to chloride free gelatin before solidification and divide in two parts. Pour commercial ferric hydroxide sol over one portion of the formed jelly and the sol well purified by dialysis over the second portion. A silver chloride precipitate occurs in the first but not in the second.

Expt. 51. Add a few drops of phenolphthalein to some aqueous NaOH. Pour this into a warm solution of gelatin in order that the jelly may appear red. Pour over the jelly some slightly acidified "alkaline blue." The rapidly diffusing hydron decolorizes the jelly and produces three patriotic layers: violet, colourless and red.

DIALYSIS

A comprehensive description of a large number of dialysers is found in Abderhalden's *Handb. d. biochem. Arbeitsmethoden*, III, 1, pp. 165-80, 1910, by E. Zunz; and in Weyls-Hauben *Methods of Organic Chemistry*, 2nd edition, 1921, 1, 428, by H. Rheinboldt.

Dialysers serve for:

1. Direct preparation of colloids.
2. Purification of large amounts of colloid material.
3. Colloid analysis, as in the determination of the dialysing properties of sols.

Graham's bell dialyser consists of parchment paper stretched over a glass cylinder.¹ R. Zsigmondy's star dialyser consists of durable parchment cups.² However,

¹ To seal the dialysing membrane to glass, use sealing wax, Chatterton rubber compound, Canada balsam, Jordis adhesive cement consisting of equal parts of collodion and concentrated alcohol or a 50 per cent. shellac solution.

² The parchment cups should not hang free, but be placed either at the bottom of the vessel or supported at the side of the dialysing vessel to prevent tearing.

pig bladders with the fat removed by ether are also used for dialysis.

Expt. 52. **Simple dialysers for preparation of colloids**—Cut out a large round sheet of parchment paper, and fold it over an Erlenmeyer or round-bottomed flask so as to form a sac. Pour the colloid into a sac, tie it with a cord and suspend it in distilled water. Change the water frequently. Place commercial 5 per cent. ferric hydroxide in the dialyser and after 1–2 hours determine the amount of chloride present in the water by means of silver nitrate. This reaction disappears after dialysing a sufficient length of time and flocculation of the sol usually occurs. Fig. 1 illustrates a better form of dialyser. Punch holes along the edge of a circular sheet of parchment paper. Pass two threads through

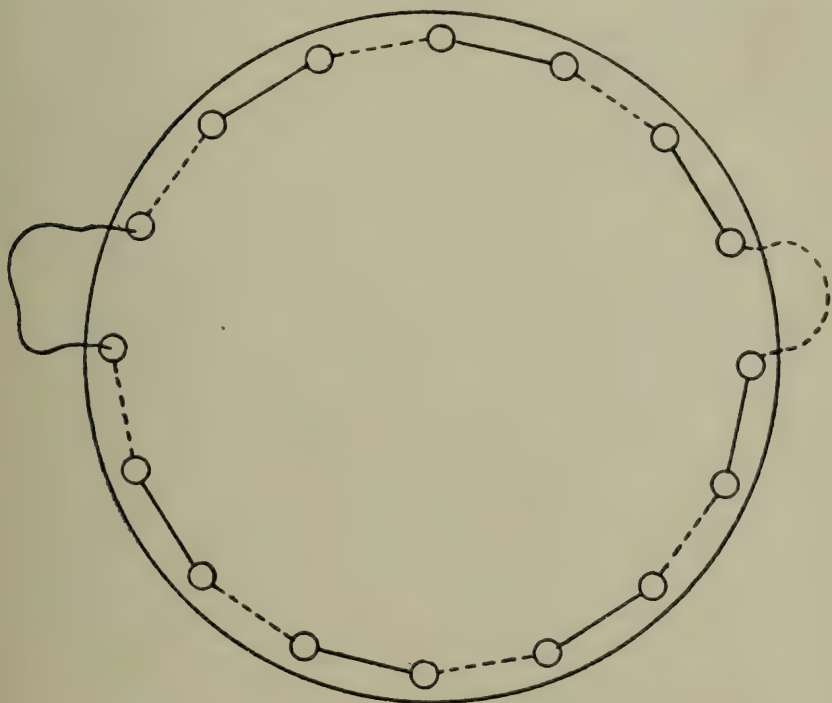


FIG. 1.

these holes similar to the drawstrings of a pouch. Moisten the paper, fold in the shape of a sac and close by pulling the threads.

Expt. 53. Make a large folded filter from parchment paper and place it in a dialysing funnel. Fasten a glass tip to the lower end of the funnel by means of a rubber tube fitted with a pinchcock. Pour the colloid about two-thirds full into the filter and cover with a glass plate or watch glass. Close the pinchcock and fill the space between the filter and the walls of the funnel with distilled water. Allow water to flow continuously into the funnel and regulate the pinchcock so that the water flows out at the same rate. By this method, comparatively large

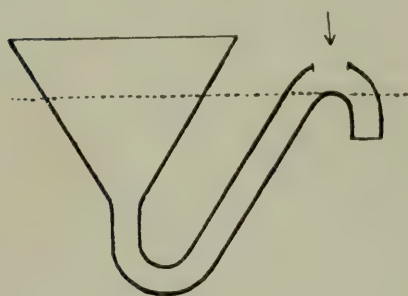


FIG. 1A.

quantities of colloid may be dialysed rapidly. The pinchcock is not necessary if a funnel is used whose tube has a double bend, as in Fig. 1A. There should be a fairly large perforation at the site indicated. The water in the funnel always has the

same level as that outside, since the perforation prevents siphoning. Place a concentrated solution of commercial "night blue" in the dialyser and detect, by means of BaCl_2 , the gradual disappearance of the Na_2SO_4 which is removed by dialysis.

These two simple dialysers may be heated at higher temperatures to obtain more rapid dialysis.

Small pieces of parchment skin are best for colloid analysis. Those prepared from the cæcum of sheep are light and thin and may be shaped in a funnel.

Expt. 54. **Simple dialysers for colloid analysis**—Take large extraction thimbles and moisten them with

warm distilled water. Drain off excess of water and while still warm fill one with a 4 per cent. collodion solution. Empty this collodion immediately into a second thimble and continue emptying into a third thimble, etc. A thin collodion layer on the wall of the cup is thus obtained. Keep all thimbles inverted so that no drops of collodion adhere to the bottom. Dry for about five minutes. Prepare in the same way, a second very thin layer, taking special care to remove excess collodion. After 5-10 minutes, immerse the thimble into cold water for about thirty minutes. These dialysers should be kept under water when not in use.

Prepare a 2 per cent. collodion solution by diluting the commercial collodion with an equal volume of 7 parts ether and 1 part absolute alcohol. Collodion of such strength forms very thin and rapidly acting dialysers.

Test the dialyser with dilute 0.05 per cent. "night blue" solution.

These dialysers are very durable and may be washed in flowing water by means of a wad of cotton. Heat does not destroy them.

Large extraction thimbles have a capacity of about 200-300 c.c. and dialysers may be made from these.

Expt. 55. Demonstration of the dialysis rates of dyes—Place three analytical dialysers in small beakers containing distilled water. Fill them three-fourths full of "night blue," Congo rubin and picric acid respectively. After twenty-four hours the "night blue" does not pass through at all; the Congo rubin but slightly and the picric acid to a marked degree.

Alternative :—Dialyse the mixture of 1 per cent. "night blue" and alkaline eosin prepared in Expt. 49. The red dye appears in the outer wash water while the "night blue" remains in the dialyser.

FILTRATION

A typical colloid, apart from adsorption, will pass unchanged through a filter paper. Hence, filter paper, clay filters, etc., are used in analytical work for the separation of typical colloids from coarse dispersions. The following table gives a list of filters with the size of pores in each.

The numbers indicate the diameter of the largest pores. The filters Nos. 602 (hard) and 602 (extra hard) are the so-called baryta filters, i.e. those which partially hold back freshly precipitated BaSO_4 and CaC_2O_4 .

SIZES OF PORES OF FILTER PAPER.

(H. Bechhold and R. Lucas.)

1450	about 4.8μ
598	„ 3.3μ
thick filter paper	„ 3.3μ
597	„ 2.9μ
602, hard	„ 2.2μ
566	„ 1.7μ
602, extra hard	„ 1.5μ
Chamberland-Kerze	„ $0.2-0.4\mu$
Reichel-Kerze	„ $0.16-0.18\mu$

Expt. 56. **Filtration of a heterogeneous disperse colloid**—Add very dilute HCl or $\text{HC}_2\text{H}_3\text{O}_2$ to a 0.1 per cent. solution of Congo rubin until the solution just assumes a violet tinge. This solution passes through ordinary filter paper. Only the red or faint violet solutions pass through filter paper of 1.5μ in diameter. The filtrates turn violet on addition of concentrated acid.

ULTRAFILTRATION

Expt. 57. **A simple ultrafilter for colloid analysis.** Fit carefully a smooth piece of filter paper into a clean

funnel, moistened well with hot water. Allow to drain. Pour 20 to 30 c.c. of warm 4 per cent. collodion over the damp filter. Rotate the funnel as rapidly as possible to obtain a primary coat of collodion upon the paper. The collodion should coat the surface of the filter paper but once, for the thicker the membrane the slower the filtration. Drain the excess collodion by inverting the filter so that no drops adhere to the tip. Allow to dry in the air for about five minutes. Remove the hardened filter paper from the funnel. Place the filter into distilled water for thirty minutes before using.

A more convenient and efficient filter may be prepared by using extraction thimbles as a support for the collodion membrane. The thimbles are of various sizes and filters of 200 to 300 c.c. capacity may be prepared.

Wash the filter with distilled water before using, in order to remove the traces of coagulated collodion. Test the filter with dilute "night blue" solution of mastic hydrosol. The filters are very durable and may be used repeatedly. Wash under a slow stream of water with a wad of cotton.

Such ultrafilters are spontaneous, that is, they filter under the pressure of their contents. It is difficult to prepare a filter of about 100 c.c. capacity which filters more rapidly than 1 to 2 c.c. per minute for colloidal solutions of the same viscosity as water. Place the ultrafilter in a funnel with a 60° cone and connect it with a section pump to hasten filtration. Too great a suction tears the point of the filter.

Use a 4 per cent. solution of collodion diluted with a mixture of 7 parts ether and 1 part alcohol, to prepare ultrafilters with a greater permeability. These membranes are thinner. A 2 per cent. collodion solution is best suited for most purposes. This provides a more permeable filter which is, however, impermeable to a

"night blue" solution. The collodion containing greater concentration of alcohol may be heated to a higher temperature. Test the permeability of the filter with several standardized freshly prepared colloidal solutions of different degrees of dispersion such as "night blue," Congo red, and collargol. A filter prepared from 4 per cent. collodion gives a clear colourless filtrate with these three dyes. A filter prepared from a 3 per cent. collodion solution retains "night blue" and often Congo red. A filter prepared from 2 per cent. collodion retains none but "night blue." These differences in permeability are due to the alcohol concentration of the collodion.

Expt. 58. **Preparation of a suction ultrafilter.** A Buchner funnel is suitable for the preparation of an ultrafilter with a large surface. This ultrafilter may be used with suction. Select a funnel with a smooth bottom. Prepare a 2 per cent. ether solution of crude rubber. Allow the solution to stand in a warm dark place, for light decomposes it. Pour about 2 c.c. of the clear rubber solution along the edge of the inclined funnel and rotate slowly. The solution yields a very thin rubber ring after evaporation of the ether. The rubber band serves the purpose of a binding rim between the porcelain and the collodion membrane, thereby ensuring a water-tight system. Collodion does not adhere to porcelain or glass. Place the funnel in a horizontal position and fit with a dry sheet of a medium-pored filter paper. Moisten the sheet with distilled water and carefully press the filter paper against the rim, keeping it free from wrinkles. Allow the paper to dry so as to decrease the tendency to warp. To remove the last trace of water, incline the funnel and absorb the collected water with filter paper. Take precautions not to tear the rubber band during the washing. Keep the funnel in a horizontal position and pour warm collodion over the paper in the manner

described above. Remove the last drops of excess collodion by inverting the funnel. A thicker collodion layer remaining in the concave edge produces leaks. After 5 to 10 minutes, pour the second collodion layer, with precautions to remove excess collodion. Dry for 10 minutes and add no more than 2 c.c. of distilled water to coagulate the membrane. Too much water will exert a greater pressure upon the soft "spongy" membrane and may destroy the efficiency of the filter. The first drops of the filtered water contain collodion. Test with "night blue" or mastic hydrosol. The filter may be washed with water and will last for months.

Rapid filtration is obtained if suction is applied to the ultrafilter on the Buchner funnel. The author could filter 200 c.c. of perfectly clear filtrate from a "night blue" solution in 1 minute. The ultrafilter lasts longer and its efficiency is greater when less suction is applied.

Expt. 59. **Ultrafiltration of disperse colloids**—Prepare several ultrafilters and set up a funnel with a paper filter alongside of each ultrafilter. Fill an ultrafilter and a paper filter with the same solutions used in Expts. 48 and 55. "Night blue," dilute India ink, dialysed ferric hydroxide, etc., pass through the filter paper unchanged. The ultrafilter retains completely the colloidal particles. Congo red and collargol are completely or partially held back, depending upon the permeability of the filter. A dilute Congo-rubin solution produces a clear filtrate at first, then the dye begins to appear in the filtrate. Molecular disperse systems, such as acid fuchsine, picric acid, methyl violet, etc., ultimately pass through an ultrafilter as easily as through filter paper.

Expt. 60. **Separation of colloids and molecular disperse phases by ultrafiltration**—Add some NaCl

or Na_2SO_4 to a "night blue" solution, ultrafilter and test the filtrate for chlorides and sulphates.

Ultrafilter commercial $\text{Fe}(\text{OH})_3$ and dialysed $\text{Fe}(\text{OH})_3$. Commercial $\text{Fe}(\text{OH})_3$ gives a yellow filtrate which is positive for ferric and chloride ions. Dialysed $\text{Fe}(\text{OH})_3$ gives a clear colourless filtrate which is but slightly positive for both ions.

Expt. 61. **Separation of dye mixtures by ultrafiltration**—Filter the dye mixtures used in Expt. 43 ("night blue" + alkaline eosin; "alkali blue" + picric acid or acid fuchsine) through a paper filter and through an ultrafilter respectively. The freshly prepared mixtures pass unchanged through the filter paper. The dark violet mixture gives a bright red filtrate with the ultrafilter; the blue or dark green mixture a bright yellow filtrate and the blue-violet mixture, a red filtrate.

Expt. 62. **Ultrafiltration analysis of a three-phase heterogeneous disperse mixture**—Add sufficient "alkali blue" to 200 c.c. of a solution of colloidal graphite in order to give the supernatant liquid a bright blue colour.

The colloidal graphite coagulates to form a coarsely disperse system. Now add saturated aqueous picric acid until the solution becomes green. Shake the mixture until the graphite gives the solution an opaque black colour. Filter three portions of this solution into Erlenmeyer flasks. The first funnel should contain a filtering cloth, the second a filter paper, and the third an ultrafilter. The filtrate in the first flask consists of the unchanged black mixture; the second filtrate, of a green dye mixture freed from the graphite, and the third filtrate, of the yellow picric acid separated from the "alkali blue."

Expt. 63. **Use of ultrafiltration in the determination of a small variation in degree of disper-**

sion. Observe that a neutral solution of Congo rubin gradually passes through an ultrafilter. Add a trace of acid to a 0.01–0.1 per cent. solution of Congo rubin to produce a blue tinge. The solution appears perfectly clear to the naked eye. Ultrafilter this blue solution. The ultrafiltrate is completely colourless or has a rose to violet tinge, depending upon the amount of acid added and the age of the blue solution.

III

SURFACE TENSION AND VISCOSITY

SURFACE TENSION

THE simplest apparatus for the determination of surface tension of colloidal solutions is a stalagmometer. It consists of a calibrated pipette with a capillary tube sealed to one end. The capillary has a fine enough bore, so that water flows out drop by drop when the tube is full. The free end of the capillary has a flat circular surface. A fluid of no surface tension would flow from this tube with a steady stream. Surface tension renders this impossible and causes the flowing liquid to accumulate into a drop which breaks when the weight exceeds the retaining force exerted by its surface tension. This force of retention is equal to the surface tension times the circumference of the drop. The greater the surface tension the greater will be the size of the drop. The number of drops of liquid obtained from a known volume of the same solution, obviously, is a measure of the surface tension of that liquid. With large drops the number is correspondingly less for a given volume of liquid and the surface tension is proportionately greater. Using the drop number of water for comparison, an increase in that number denotes a decrease in the surface tension, while a decrease in the drop number denotes a corresponding increase. This method gives relative values for surface tension, adequate for most studies of colloidal solutions.

Surface tension decreases but slightly with increase of temperature, therefore temperature control is not necessary for most experiments. On the other hand, the surface tension varies with the rate of dropping, because the drop number tends to be greater for a slower rather than a faster rate of flow. Equal rates of the dropping are necessary for accurate measurements.

Take a 3 or 5 c.c. graduated pipette and attach a piece of capillary tube to one end by means of a rubber connection. The capillary must be of sufficient length and of suitable bore so that the liquid flows by drops when the pipette is full. The free end of the capillary must be ground flat. Suspend the pipette at such a height that a dish or an Erlenmeyer flask may conveniently catch the falling drops. A greater number of drops per unit volume, 124 instead of 120, is obtained when the pipette is inclined. Fill the pipette above the upper mark and begin counting the drops released when the meniscus just passes it. The accuracy of the results increases with the increase of absolute drop number, hence the volume used should yield more than 100 drops.

Expt. 64. **Surface tension of soap solutions**—Prepare a 0.1 per cent. solution of any soap. A soap solution gives a drop number of 90 or more, while pure water gives about 60 per unit volume. Measure the drop number of intermediate concentrations to determine the minimum concentration of soap necessary to produce a considerable decrease in surface tension.

Expt. 65. **Stalagmometric studies of colloid**



FIG. 2.

chemical reactions (J. Traube).—Measure the drop number of a 0.2 per cent. “night blue” solution. It is higher than that of pure water. Add the following amounts of KI to 10 c.c. of “night blue” solution :

	Substance added.	Examples of Drop Number Values.
Water	—	124
0.2 per cent. “night blue” .	—	144
10 c.c. “night blue”	+ 5 drops 0.001N KI	142
“ “	+ 1 drop 0.01N “	140
“ “	+ 2 drops 0.01N “	130
“ “	+ 5 “ 0.01N “	120
“ “	+ 1 drop 0.1N “	119
“ “	+ 1 “ 0.1N “	127
“ “	+ 2 drops 0.1N “	126
“ “	+ 6 “ 0.1N “	125
	Flocculation.	
Water	—	124

The following numbers are obtained by using KBr instead of KI :

	Substance added.	Drop Number.
Water	—	124
0.2 per cent. “night blue” .	—	144
10 c.c. “night blue”	+ 1 drop 0.1N KBr	137
“ “	+ 1 “ “	124
“ “	+ 1 “ “	119
“ “	+ 2 drops “	117
“ “	+ 2 “ “	116
“ “	+ 3 “ “	131
“ “	+ 6 “ “	128
“ “	+ 8 “ “	127
“ “	+ 15 “ “	126
“ “	+ 30 “ “	125
	Flocculation.	

The effect of alkali halogens upon the surface tension

of "night blue" is shown in Fig. 3. Flocculation of the dye occurs just before the drop number for water is reached.

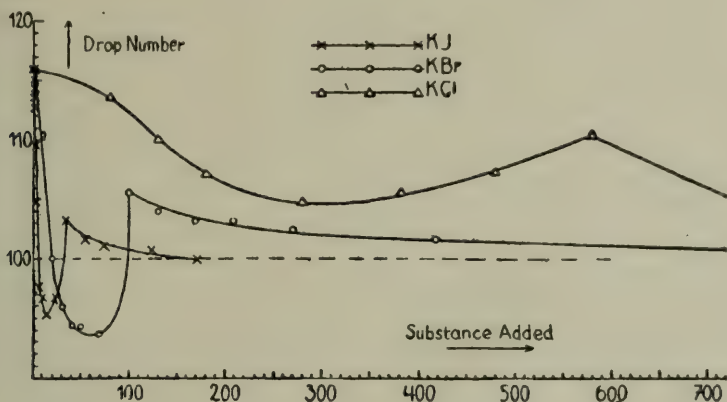


FIG. 3.

VISCOSITY

Viscosity denotes the resistance which a fluid exerts against displacement of its own molecules. Glycerin has a high viscosity and ether a very low one. An approximate measure of this value is the time a given volume of liquid requires to flow through a certain capillary. Relative viscosity suffices in colloid chemistry. It is proportional to the product of the time of flow, the specific gravity of the substance and the so-called apparatus constant, K . This is determined by standardizing the viscosimeter in terms of distilled water. Generally, the specific gravity may be neglected. If the viscosity of water, observed in the apparatus, be assumed unity, the relative viscosity of the colloid studied is simply the ratio of the time of flow of the colloid to that of water through the viscosimeter. The viscosities of many homogeneous liquids are independent of the

pressures which produce the capillary flow. However, the viscosity is affected appreciably at higher pressures, of course in the direction of a faster rate of flow. The work of E. Hatschek, W. Hess, and E. Röthlin shows that the viscosities of hydrophile colloids deviate from Poiseuille's law with slight variations. Hence, even relative viscosity measurements must be made at known or constant pressures.

The Ostwald viscosimeter is a very convenient form of apparatus. It consists of a U-tube, one arm



FIG. 4.

of which has a capillary and bulb. The two ends of the bulb are marked so that it may contain a definite volume (Fig. 4). In using the viscosimeter, always place the same volume of liquid in the tube, draw it into the capillary side arm above the upper mark, and measure the time of flow of the liquid between the two marks. Use a viscosimeter with a capillary of greater bore for viscous liquids, such as hydrophile emulsoids. Viscosimeters whose capillaries permit the volume of water between the two marks to flow out within 20 seconds are most suitable.

The viscosity of a liquid varies considerably with the temperature, hence the viscosimeter should always be kept in a water-bath with two glass sides so that the flow of the liquid may be observed. The viscosimeter should be cleaned by drawing cleaning mixture and water through the capillary. The presence of gas bubbles in the capillary prevents adequate cleansing of the viscosimeter wall, and therefore inaccurate measurements result. This viscosimeter may be more conveniently used by providing the side arm with a rubber stopper containing a bent glass tube. Attaching a piece of rubber tubing to the glass tube, the liquid within

the viscosimeter may be blown into the capillary and back with each measurement.

VISCOSITY EXPERIMENTS WITH GELATIN SOLUTIONS

Gelatin is a hydrophile emulsoid which has been studied more extensively than other albuminous substances. Prepare a 1 per cent. solution of gelatin in the following manner: Weigh 2 g. of either sheet gelatin, gelatin cuttings used for photographic purposes or gelatin powder and place it in cold distilled water. Change the water often in order to obtain a "pure" solution. Weigh a beaker, add 150 c.c. of water and heat to boiling. Remove the flame and add the swollen gelatin free from wash water. Stir continuously with a glass rod until the gelatin dissolves. The decomposing effect of heat as well as the stickiness of the gelatin are thus avoided. After the gelatin dissolves, cool and weigh the beaker and contents. Add enough water to obtain 200 g. of a 1 per cent. solution.

Pass water at room temperature through the viscosimeter at least 30 to 40 seconds before measuring the viscosity of the gelatin.

Expt. 66. Influence of the age of gelatin solutions upon viscosity—Measure the viscosity of the cooled gelatin solution directly after preparation. Measure it again in half an hour. The solution may be left in the viscosimeter, but must be drawn two or three times through the capillary before making a measurement. The viscosity of the solution increases considerably after standing an hour. A 1 per cent. solution is usually too viscous to flow through the viscosimeter.

Expt. 67. Influence of preliminary mechanical treatment on the viscosity of gelatin solutions—

Allow a 0.5 per cent. gelatin solution to stand in the viscosimeter for 24 hours. Measure the viscosity after drawing the solution very slowly into the capillary. Then agitate the solution by rapidly drawing it through the capillary several times or by bubbling air through it. Measure the viscosity once more and observe a considerable shorter time of flow.

The structure of a very dilute gelatin solution is the cause of these phenomena. Therefore, it is necessary to run the solution through the viscosimeter two or three times before determining the viscosity of the colloid.

Expt. 68. **Influence of preliminary thermal treatment on the viscosity of gelatin solutions**—Measure the viscosity of a 0.5–1 per cent. gelatin solution. Place about 200 c.c. of this solution in an Erlenmeyer flask and heat on a steam-bath. Provide the flask with a reflux condenser to prevent loss of water by evaporation, or mark the original water level, and after heating add the required amount of water. Remove every half-hour about 20 c.c. of solution and determine after cooling the viscosity of this sample.¹ Do not forget to replace the water lost by evaporation. To obtain more accurate results, heat a larger volume of gelatin solution and take larger test portions. Use these portions to determine the increase of viscosity with time. Plotting the viscosities obtained as ordinates against the age of the solutions as abscissæ, a series of curves are obtained in which the gelatin solutions which have been heated the longest, show the lowest slope. For longer periods of heating the gelatin solutions, the slopes of the age curves approach zero.

¹ The concentration of the solution can be maintained fairly constant by weighing the filled flask before and after heating as well as before and after removing samples and subsequent refilling.

- { 5a. 20 c.c. 1 per cent. gelatin + 16 c.c. H_2O + 4 c.c. 0.1N
 NaOH = about 0.01N NaOH.
 { 5b. " " " " + 16 c.c. H_2O + 4 c.c. N NaOH
 = about 0.1N NaOH.

Mix the solutions thoroughly and allow them to stand for 24 hours. Determine rate of flow, or better still, determine the age curves in the manner described above (Expt. 68).

The addition of sulphates to a gelatin solution increases its viscosity considerably compared with that of pure gelatin. The iodides and bromides greatly decrease the viscosity. Carbonates, phosphates, oxalates, acetates and citrates raise the viscosity. The cyanides and thiocyanates lower it. Chlorides, nitrates, and chlorates form complex changes, in so far as they can raise or lower the viscosity according to their concentration and the age of the gelatin.

Additions of acids and bases, in the small concentrations mentioned, increase the viscosity. Greater concentrations lower it again. A viscosimeter having a rate of flow for water equal to 150 fifth-seconds, gives the following values: 700 for a 0.5 per cent. gelatin solution; 3-4,000 for 0.005N HCl; 300 for 0.1N HCl; 2-3,000 for 0.01 N NaOH; 500 for 0.1 N NaOH, etc. Prepare the complete concentration curves for HCl, NaOH and NaCl, and determine the viscosity 24 hours after preparation of the mixtures.

VISCOSIMETRY OF CHANGES OF STATE OF AGGREGATION

Expt. 72. **Viscosity measurements on the coagulation of aluminium hydroxide hydrosol**—Measure the viscosity of a highly concentrated $\text{Al}(\text{OH})_3$ sol prepared according to Expts. 30 and 34. The viscosity of

this sol is higher than that of water, hence use a viscosimeter of wider capillary bore. Mix 8 c.c. of the sol with 2 c.c. of 2N KCl¹ and measure the changes in viscosity with time. Such an experiment gave the following results :

Original Value	393	fifth-seconds
After 15 minutes	406	„
„ 55 „	417	„
„ 90 „	427	„
„ 160 „	445	„

Coagulation depends upon the concentration of the sol and that of the added solutions. After coagulation, the viscosity of the system again decreases and after 16 hours the vigorously stirred solution gives a rate of flow equal to 415 fifth-seconds.

Expt. 73. **Viscosity measurements of the setting of plaster of Paris** (Wo. Ostwald and P. Wolski, *Kolloid. Z.*, 27, 78 (1921)—Prepare a 5 per cent. suspension of finely powdered gypsum and transfer at once to a viscosimeter. Sedimentation may be prevented by drawing a continuous current of air through the suspension. Ob-

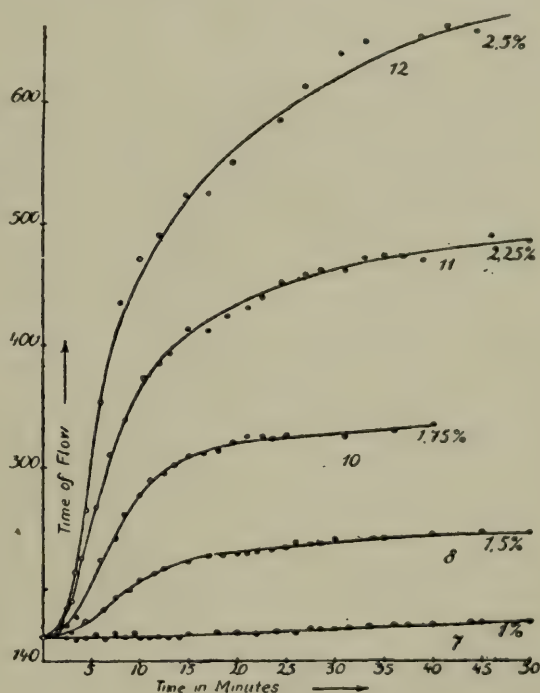


FIG. 5.

¹ Use an empirically determined KCl concentration which will produce no flocculation within a half-hour.

serve that the viscosity increases with the time as shown by Fig. 5. The process of setting may thus be followed by viscosity measurements. A viscosimeter having a diameter of 0.7–1.0 mm. and a water value of 100–150 fifth-seconds is suitable for a charge of 20 c.c.

Expt. 74. Viscosimetry of the formation of potato starch paste—Suspensoid systems, such as coarse suspensions of starch in cold water, show relatively small increases in viscosity, approximately proportional to their concentrations. On the other hand, hydrophile emulsoids show very great increases in viscosity both absolutely and relatively, with increases in concentration. In the formation of potato starch paste, which, as is well known, generally takes place between 55° and 65° C., a suspensoid system is converted into an emulsoid one. On warming the starch suspension, the viscosity decreases in accordance with the known decrease in the viscosity of water, the dispersion medium. When the temperature is raised between 55°–65° C. this decrease is, however, replaced by a great increase in viscosity, the most striking criterion of the formation of paste and of a radical change in the starch-water system.

In order to measure the viscosity of a dispersoid which coalesces spontaneously after the fashion of unheated starch suspensions, a viscosimeter must be used whose rate of flow is relatively large compared to its rate of sedimentation.¹ Suitable viscosimeters have small volumes and short narrow capillaries or larger volumes and longer capillaries of wider bore. A 0.5–1.0 per cent. starch suspension may be used in the first type of viscosimeter, whereas a 5 to 10 per cent. starch suspension is suitable for the second type.

Warm the starch suspension in the viscosimeter in a water-bath with glass walls (a large beaker). Place the

¹ See Wo. Ostwald and H. Luers, *Kolloid. Z.*, 25, 82, 116 (1919).

thermometer in the liquid contained in the wide side arm of the U-tube, for the temperature of the suspension lags behind that of the water-bath. Warm the starch suspension rapidly to 50° C., measuring the rate of flow every 10° . Above 55° C. warm the suspension slowly at a rate of about 1° C. per 5 minutes. Lower the flame, measure the rate of flow continually and record the temperature of the water-bath after stirring. Stir the starch suspension thoroughly, by bubbling air through it before each measurement. If the concentration and the capillary bore of the viscosimeter have been suitably chosen, we find within a narrow temperature interval a change from decrease of viscosity to an increase as given in the following example :

Five per cent. suspension of commercial potato meal ; small viscosimeter, water value about 365 fifth-seconds at 25° C. Charge, 10 c.c.

Temperature.	Time of Flow (T).	Log. T.
55.3	230	2.36173
55.5	228	.35793
56.2	226	.35411
56.6	225	.35218
57.3	224	.35025
57.7	221	.34439
58.1	220	.34242
58.4	220	.34635
58.8	228	.35793
59.4	235	.37107
59.5	240	.38021
59.7	244	.38739

Between 58.1° and 58.4° C. there is a reversal of the viscosity change, i.e. the formation of starch paste. A graphical representation of the formation of starch paste

is given below in another experiment. If the viscosimeter is not sensitive or the concentration of the starch suspension too small, the time of flow neither decreases nor increases, but remains practically constant within a range of 10°C . as in the following experiment:

A 5 per cent. suspension of potato meal; viscosimeter too large, water value about 150 fifth-seconds at 25°C .; charge, 20 c.c.

Temperature . .	41	49	53	55	57	59	61	63	64	65
Time of Flow . .	112	106	103	101	100	100	100	100	101	113

For a more accurate determination of the temperature of starch paste formation, it is necessary to select a suitable viscosimeter so that the point of inflexion is observed within a very narrow temperature range.

Furthermore, it is observed that in going above the temperature of starch paste formation, the times of flow determined in rapid succession are no longer constant but increase spontaneously because starch paste formation requires a certain amount of time. Such an observation can of course be utilized as an approximate indicator of the temperature of starch paste formation by determining at which temperatures there are definite increases in viscosity according to three consecutive measurements made within 10 minutes. The use of a sensitive viscosimeter is of course more accurate and more rapid.¹

To determine the exact temperature of starch paste formation, graphic representation of the data may be made in the following way: Plot the temperatures as abscissæ and the logarithms of the times of flow as ordinates. From the data in the above table are obtained

¹ Such experiments demonstrate that a definite temperature of starch paste formation in a physico-chemical sense is a practical entity. Strictly speaking, there is probably a temperature range in which the rate of starch paste formation is abnormally rapid.

two practically straight lines (Fig. 6), which produced, intersect at a point.¹ This experiment gives graphically a temperature of starch paste formation between 58.2° – 58.3° C. If the graph of data obtained shows a horizontal line connecting the two oblique branches, it is due to the use of an unsuitable viscosimeter or to too small a concentration of starch suspension. In such a case the two lines may be produced until they intersect at a point which would give an approximate value of the temperature of starch paste formation.

Expt. 75. Viscosity measurements of the ageing of starch paste (M. Samec).

—Prepare a 1 per cent. starch solution by moistening 4 g. of potato starch with a small amount of water and add gradually with constant stirring,

200 c.c. of warm but not hot water. Dilute to twice the volume, boil on a sand-bath for 30 minutes and after cooling make the volume up to 400 c.c. Filter and cover with toluene for protection against bacterial action. Determine the time of flow for this suspension immediately after preparation. Measure the rate of flow of this suspension every day and plot the rates of flow against age. On plotting the viscosities obtained, the curve shows a large decrease in viscosity at first and gradually becomes asymptotic after an ageing of one to two weeks.

Expt. 76. Viscosity measurements on the coagulation temperature of an albumin solution—Separate the yolk of a fresh egg from the white. Beat the latter into a foam and allow to stand overnight. The greater

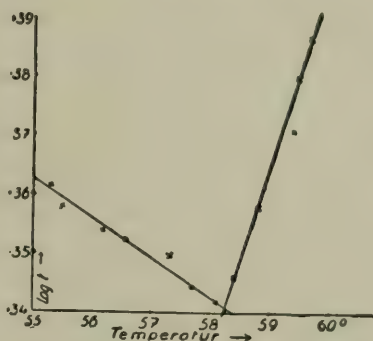


FIG. 6.

¹ Another example is given by Wo. Ostwald, *Koll. Z.*, 12, 215 (1913).

part of the foam clears while the egg membrane remains suspended in the remainder of the foam. One egg gives about 20 c.c. of liquid, which is a mixture of albumin, and globulin. Dilute to twice the volume with a weak solution of 0.7 per cent. NaCl. The solution becomes turbid upon dilution with distilled water due to the relative insolubility of the globulin. Measure the change in viscosity with rise in temperature under the same conditions as those of the starch paste in Expt. 74, using the same rates of temperature increase. The time of flow decreases at first with rise in temperature until about 60° C. is reached, then either an increase or no change in time of flow occurs, depending upon the concentration of the solution and the sensitivity of the viscosimeter. The time of flow decreases again when the temperature exceeds 70° C. Observe that

Temp.	T. for egg white.	T. for water.	Δ
51.0	311	233	78
55.0	292	220	72
56.3	286	217	69
57.0	283	215	68
57.6	281	213	68
58.3	277	212	65
59.2	275	210	65
60.3	270	206	64
61.0	267	205	62
61.6	268	204	64
62.6	267	202	65
62.8	267	200	67
63.5	266	199	67
63.7	267	198	69
64.5	266	196	70
66.0	252	192	60
66.9	247	190	57
69.5	238	185	53

the solution becomes turbid during the increase in the times of flow.

The viscosity change during coagulation may be made more obvious by plotting the viscosity increase (i.e. time of flow of solution minus time of flow of H_2O at the corresponding temperature) instead of the rate of flow as observed. This may be done by plotting a temperature—viscosity curve for water in the same viscosimeter. Compare the rates of flow of water with those of the egg white solution at the corresponding temperatures and plot in the same manner. A simple illustration of such an experiment is given graphically in Fig. 7,¹ wherein the differ-

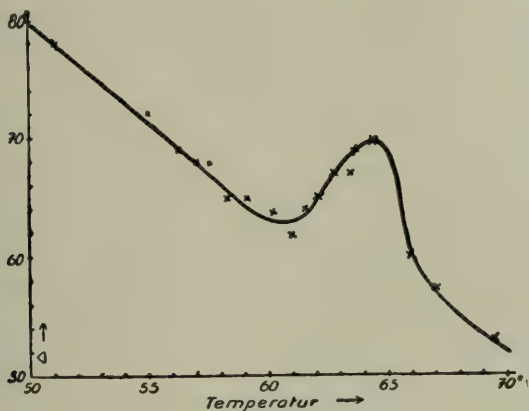


FIG. 7.

ences in viscosities between albumin and water are plotted for increasing temperatures. The experiment was performed with equal volumes of egg albumin and 0.7 per cent. NaCl solution. The viscosimeter was of the small type with a water-value of 365 fifth-seconds at 25° C.

The curve and data show that the coagulation of the albumin solution takes place at about 61° C. By plotting

¹ Another example is given by Wo. Ostwald, *Koll. Z.*, 12, 214 (1913).

the logarithm of the rate of flow against the temperature, two approximately straight lines are obtained which intersect to give an acute angle. The determination of coagulation temperatures is practically conclusive only when all experiments are conducted under similar conditions. The viscosimetric method may be used to study the kinetics of effects of added salts, acids and bases on the course and mechanism of coagulation at the critical temperature range.¹

¹ More specific data is given in the monograph by H. Chick and C. T. Martin, *Kolloidchem. Beihefte*, 5, 49 (1913).

IV

OPTICAL PROPERTIES

OPTICAL HETEROGENEITY

THE optical heterogeneity of solutions is shown macroscopically by turbidity, microscopically by the so-called ultramicroscopic phenomena.

Turbidity is best observed by contrast against a dark background. Better results may be obtained by placing a source of intense illumination to one side of the dark background or by holding the test-tube in a narrow beam of sunlight or a beam from a projection lamp. For ordinary purposes wrap a piece of black paper with a small hole in it around an incandescent lamp. The light from the source of illumination should not fall directly on the eye of the observer.

For semi-quantitative purposes, prepare a comparison scale with milk or mastic hydrosol.¹ Start with a concentrated milk-white sol and dilute to give the required turbidity. A mastic sol is remarkably stable for determinations of the turbidity of colourless sols provided an aged sol is used. Nephelometers, Tyndallometers² and

¹ Diluted milk is especially suitable as a standard since the measurements of N. Mänz (*Dissertation*, Marburg, 1885) showed that it absorbs all wave-lengths equally. F. B. Young [*Phil. Mag.* [6] 20] 793 (1910)] used diluted milk as a standard for degrees of turbidity of ether at the critical temperature.

² See B. H. von Oettingen, *Z. f. physik. chem.*, 33, 1 (1900); J. Friedlander, *ibid.*, 38, 385, 413 (1900); C. Benedicks, *Koll. Z.*,

also colorimeters may be used for more accurate determinations of turbidity,¹ which is the ratio of the light diffracted by the colloid particles to that transmitted.

Expt. 77. Detection of faint turbidity by means of the Faraday-Tyndall light cone—A large number of disperse systems appear completely transparent upon superficial examination, especially in transmitted light. However, they produce a decided Tyndall effect. Examine the following sols by transmitted light and then by a narrow beam of light from a projection lantern: a red gold sol, freshly dissolved collargol, freshly prepared arsenic trisulphide or Prussian blue, as well as a 1 per cent. solution of potato starch paste which has been heated for thirty minutes.

A cold saturated solution of cane sugar gives a bluish-white light cone:

Expt. 78. Polarization of the Tyndall light cone—Place a turbid colloidal solution as mastic hydrosol in the beam of a projection lantern. Use a sol of such dilution that it will give a well-defined Tyndall cone unaffected by too an intense source of light. Examine this cone with a Nicol prism at right angles to the beam of light. The cone of light disappears or becomes dim twice

7, 204 (1910); Th. W. Richards, *Proc. Amer. Ac.*, 30, 385 (1904); *Am. Chem. J.*, 31, 235 (1914); 35, 510 (1906); R. C. Wells, *ibid.*, 35, 100 (1906); E. Schlesinger, *Berl. Klin. Wochenschr.*, 48, 42 (1911), etc.; accurate measurements are given by W. Steubing, "On the optical properties of colloidal gold solutions," *Dissert.*, Greifswald (1908); *Ann. d. Physik*, 26, 329 (1909); W. H. Keesom, *Ann. d. Physik*, 35, 591 (1911); *Comm. Phys. Lab.*, Leyden, No. 104 (1910); W. Mecklenburg and S. Valentiner, *Z. f. Instrumentkunde*, 34, 209 (1914); *Kolloid. Z.*, 15, 99 (1914); 16, 97 (1915); F. Sekera, *Koll. Z.*, 27, 28 (1921); H. Kleinmann, *ibid.*, 27, 236 (1921).

¹ An apparatus like the Wilh. Ostwald-Donnan's Colorimeter is suitable (*Physico-chemical Manual*, 3rd Ed., 358 (1910)).

in one complete revolution of the prism. The light is thus partially polarized. Perform similar experiments with a very dilute solution of a fluorescent substance, such as quinine sulphate, alkaline fluorescin or eosin and observe that no dimming of the light cone occurs by revolving the prisms. Fluorescent light in distinction from a light ray of a turbid solution, is not polarized.

Expt. 79. **Turbidity and degree of dispersion**—Experiment and theory show that turbidity is greatest in a solution of moderate concentration of the disperse phase. Therefore, the maximum degree of turbidity does not occur in colloids, but in coarsely disperse systems.

Place freshly prepared mastic, arsenic trisulphide or red gold sol in two beakers and to one add a few drops of HCl or BaCl_2 solution. Compare the turbidities by means of a Tyndall cone and observe that the coalescing sol shows a considerably greater turbidity.

Perform the same experiments with dilute "Congo rubin." The "pure" solution seldom shows a light cone in a nephelometer. Add a few drops of an electrolyte as HCl, $\text{Ba}(\text{OH})_2$, until the solution gradually changes to a blue-violet colour as the turbidity increases. The coagulated sols show individual coarsely disperse particles when shaken. The diffracted light which these coagulated particles radiate is less intense than during the initial stages of flocculation.

TURBIDITY PHENOMENA IN HYDROPHILE COLLOIDS

Changes in turbidity are not only dependent on the variation in the degree of dispersion but also on the degree of hydration. Every emergent ray from a colloid solution whether produced by refraction or reflection, is due to a distinct variation in the optical relations between

the disperse phase and the dispersion medium. This difference is less the more hydrated is the disperse phase. The difference increases if dehydration of the disperse phase takes place. Variations in the degree of dispersion and hydration frequently occur at the same time. Marked variation in the turbidity of a colloid solution may occur with but slight changes in external conditions.

Expt. 80. **Changes in turbidity of aqueous gelatin solutions with concentration**—Prepare a series of gelatin solutions¹ of the following concentrations by diluting with warm water :

6 4 3 2 1.5 1 0.5 per cent.

After the solutions have cooled allow to stand overnight in an ice-box. The maximum turbidity occurs not in the most concentrated solution but in the one of medium concentration such as 2–3 per cent. Gelatin solutions prepared at a lower temperature show the turbidity maximum more distinctly.

Soak a thick sheet of gelatin or a transparent sheet of glue in a beaker filled with water. After a few hours, compare the soaked swollen portions with those still unaffected. Observe that a considerable increase in turbidity has occurred in the portion swollen by the water. Dry a piece of 30 per cent. gelatin jelly in an oven or in a desiccator over H_2SO_4 . Do not use too high a temperature when drying with heat on account of the tendency of the gel to liquefy. The 30 per cent. gelatin jelly is very turbid, but it becomes less so with gradual loss of

¹ The gelatin is purified by washing for 2–3 days with continuously flowing water or by frequently replacing with distilled water, and the weight of the gelatin determined before and after swelling with the added precaution that none of the gelatin is lost during the washing. The latter may be realized, in the author's experience, by using boiled porous sacks. The experiment may at times be carried out with unwashed gelatin.

water and finally almost transparent when the original thickness of the gelatin is attained. Therefore a gelatin-water mixture of various concentrations may have two degrees of maximum turbidity.

Expt. 81. Effect of dehydration on turbidity of silicic acid gels—Prepare according to Expt. 25 a clear aqueous solution of silicic acid by mixing two parts of 2N acetic acid with one part of water, and after cooling the mixture, carefully add one part of 10 per cent. water glass.¹ Place the greater portion of this gel in a desiccator over concentrated H_2SO_4 . This dries in the course of 1 to 2 weeks at a rate which may be determined by periodic weighings. Observe that with a water content of 35–55 per cent., the apparently clear jelly containing some gas bubbles gradually becomes turbid. Generally, the centre of the jelly mass first shows an opalescence which gradually extends in all directions. This illustrates the sudden “transitions” of the silicic acid gel. The turbidity disappears after longer desiccation and the jelly becomes as transparent and as firm as glass.² If a dried piece of jelly is placed in a flask with moistened filter paper and the flask sealed with a stopper, the hardened gel frequently disintegrates with a noise as a result of internal stress. Such gels usually show a new “transition” after rehydration but not to as marked a degree.

Expt. 82. Gelation and turbidity—Allow one portion of a 2–3 per cent. gelatin solution to solidify at room temperature, another portion in an ice-chest and

¹ Acetic acid yields as a rule clearer gels than HCl.

² Good results have not always been obtained by the author, as J. M. van Bemmelen has already reported. Occasionally the author has been able to observe the phenomenon on drying the silica gel, previously washed with HCl, in the air and also warming it gently. Sometimes, in spite of apparently similar conditions, the phenomenon has not been observed; however, it may have been missed during the night.

keep the remainder liquid at about 30° – 40° C. The solution which solidifies most rapidly at a low temperature is the most turbid and that solidifying at room temperature is more turbid than the fluid solution at an elevated temperature.

Fill two beakers with the same 2–3 per cent. gelatin solution, liquefy both portions by placing them in hot water for about 30 minutes. This liquid jelly is much more turbid than the solid portion.

Expt. 83. **Ageing phenomena and turbidity**—Let a 1 per cent. solution of starch paste age in an ice-chest (Expt. 75). The freshly prepared solution shows a bluish-white opalescence. Its turbidity increases considerably upon ageing and in the course of 2–3 weeks it becomes white and opaque. A considerable increase in turbidity of the jelly is observed after 24 hours.

Expt. 84. **Influence of electrolytes upon the turbidity of gelatin jellies**—Prepare about 150 c.c. of 2–3 per cent. gelatin solution. This concentration of jelly shows the maximum turbidity (Expt. 80). Pour 10 c.c. of this solution into a number of test-tubes and add to successive portions a drop of 2N solutions of NaOH, KI, KNCS, KCl and Na_2SO_4 so that a 0.01N solution results. Place these tubes in the ice-box, as well as two control tubes which contain no additions. The following series of decreasing turbidities are observed after 1 to 2 days:

Control, KI, KNCS, KCl, Na_2SO_4 , HCl, NaOH.

All electrolytes in the concentrations given above produce a decrease in the turbidity of the jelly. Acids and bases exert the strongest effect.

Expt. 85. **Critical turbidity**—A distinct turbidity maximum is observed at an intermediate stage of mixing two liquids soluble in one another to a limited extent (J. Friedländer, V. Rothmund). Prepare a mixture of

about 36 parts of colourless solid phenol and 64 parts of water. At room temperature, there are two layers, which form molecular disperse immiscible systems. Heat the mixture to 70°C . and shake continuously until the turbid emulsion becomes clear. Continue to shake the solution and allow it to cool slowly. At first a very slight turbidity occurs which appears as a colour phenomenon or as an opalescence. This is indicative of the emulsoid state.¹ On further cooling the turbidity increases considerably and a coarsely disperse emulsion appears which gradually separates into two distinct layers.

ULTRAMICROSCOPY

According to the theory of microscopy, particles appearing geometrically similar are greater than the wave-length of light to which they are exposed. Such particles may be differentiated from one another provided they are spaced at intervals greater than one-half the wave-length of the light by which they are illuminated. The smaller colloidal particles have the dimensions of about 0.1μ , and hence cannot be optically distinguished with an ordinary microscope. However, it is possible to distinguish single colloidal particles without their individual geometric forms by means of an intense lateral illumination and not by transmitted light. By this method, particles which are considerably smaller than the wave-length of light may be recognized individually, for they reflect the light in all directions and are consequently self-illuminative.

An ultramicroscope consists of an intense Faraday-Tyndall cone which strikes a microscope with a special attachment to make colloid particles visible.

Water for ultramicroscopy—Water with the least

¹ See Wo. Ostwald, *The World of Neglected Dimensions*, 8th edition (Dresden, 1922), p. 72.

amount of optical impurities is obtained by storing a large volume of distilled water at a uniform temperature for a long period of time and then siphoning off the upper portion of the water. Glass and hard rubber stoppers give "optical dust" which may be prevented by covering the stoppers with paraffin or tinfoil. Ultrafilters improve the water considerably, especially if the water is carefully excluded from the air after filtration. The number of dust particles present is usually small and the experimenter soon learns to recognize their presence.

Expt. 86. **Suspensoids**—Ultramicroscopic experiments may be easily performed on the separate particles of suspensoid colloids, if the distance between each particle is relatively great. The colloidal solution must be very dilute so that the particles are at sufficient distances from each other, to obviate mutual reflection phenomena which would blur the particles when viewed individually against a dark background.

Mastic hydrosol—A very dilute sol prepared according to Expt. 1 shows a large number of white, intensely illuminated particles in rapid Brownian movement. The interference of aggregated particles is certainly appreciated if observations are made after alternate additions of the concentrated solution and distilled water. A dark background is necessary for the easy detection of the individual particles.

Black India ink gives an image similar to mastic sol when using a much greater dilution. The background cannot be made so dark because of the presence of hydrated or protective colloids. Both the black and colourless particles reflect white light.

Gold hydrosol—Observe and compare ultramicroscopically the red and blue gold sols prepared according to Expts. 2-7. Smaller particles are usually found in the red sol rather than in the blue sol unless the red sol is

prepared in the presence of protective colloids. Red sols occasionally show larger particles, which probably are soluble aggregates of smaller particles. A highly disperse dilute gold sol cannot be further resolved ultramicroscopically, but gives only a diffused light cone.

Other experiments on suspensoids—Colloidal silver and other metal sols¹; Prussian blue, metallic sulphides, organic dyes such as indigo, alkali blue, alizarin in paste form are suspensoids which are suitable for ultramicroscopic experiments.

Quantitative studies of the dimensions of particles cannot be based upon the size and intensity of the illuminated spots observed. For experiments on approximate determinations of particle size, see H. Siedenkopf and R. Zsigmondy, *Ann. d. Phys.*, **10**, 16 (1903); G. Wiegner, *Koll. Beih.*, **2**, 213 (1911). Particles of microscopic dimensions, those of 0.2μ and more in diameter, are recognizable by the formation of refraction figures, such as concentric circles, V- or Y-shaped light haloes and other complicated light figures. Typical colloidal suspensoid particles produce comparatively bright and approximately circular light areas.

Emulsoids—Non-hydrated emulsoids such as oil-water sols (Expt. 1) give the same ultra-images as suspensoids. The difference in optical constants between the disperse phase and dispersion medium, which are necessary for ultramicroscopic recognition of the particles, disappears with increasing hydration. The undifferentiated light cones always become dimmer with increasing hydration of the suspensoid and may practically disappear. Such negative results are due to smaller particles in the emulsoid previous to hydration. One must distinguish between an optical amicroscopy and a dimensional amicroscopy. A negative ultramicroscopic obser-

¹ Compare the preparations given in Chapter IX.

vation does not prove the presence of a highly disperse emulsoid. Many solutions may be recognized as colloid systems in consequence of diffusion, dialysis, ultrafiltration, etc., yet they give only a negative or diffuse ultramicroscopic image. Starch paste is a good example of such an emulsoid.

Ferric hydroxide sols—These sols are transitions between suspensoids and emulsoids, and illustrate emulsoid properties even better than solutions of egg white, gelatin, etc. Ferric hydroxide does not contain so many coarse impurities as the viscous albumin and gelatin sols. Sols which prove to be typical colloids by dialysis or ultrafiltration show at first an increase in light intensity, but on further dilution they show a light cone not resolvable into single particles. The commercial $\text{Fe}(\text{OH})_3$, or preferably that prepared in Expts. 21 and 22, is suitable for these experiments.

Solutions of egg white, gelatin, silicic acid, stannic acid, etc., usually show a diffuse cone containing much "optical dust."¹ A 0.5–1.0 per cent. solution of potato starch which has been heated at 100°C . for 30 minutes appears relatively clear. Starch paste shows a considerably diffuse light cone, in which only few "dust" particles are imbedded. If the starch sols are heated at 100°C . for about 10 minutes, they coagulate and show a greyish-white irresolvable light cone. Nevertheless, the starch particles are not so coarse to settle on standing. This is an example of the above-mentioned fallacy of assuming dimensional amicroscopy from optically clear images given by sols whose particles are irresolvable. In previous experiments the starch particles were apparently so

¹ Optical and chemical purity are not necessarily equivalent. Sodium hydroxide may be prepared with the greatest precaution from fresh metallic sodium and yet may not be optically as clear as an old caustic solution whose impurities have settled.

strongly hydrated, especially in their external layers, and were so thickly aggregated that the optical transition between disperse phase and dispersion medium was practically constant. Dyes such as safranine, night blue, etc., usually contain so many impurities that they tend to destroy the typical image of an irresolvable light cone.

Freshly prepared, very dilute silicic acid and solutions which contain great excess of acid appear optically clear. This also applies to serum and egg albumin solutions to which a few drops of HCl or NaOH have been added.

ULTRAMICROSCOPIC CHANGES OF STATE

The large number of experiments on turbidity phenomena described in the previous paragraphs (77-85) may also be performed ultramicroscopically by observing changes of state in colloidal solutions.

Expt. 87. **Ultramicroscopy of gelation**—According to the experiences of the author a solution of “pure” gelatin is essential for an accurate study of the changes of state. This solution is best prepared by washing a 2-3 per cent. gelatin for several days.

This lukewarm¹ solution shows a grey-white Tyndall cone containing many impurities and showing Brownian movement. Choose an ultramicroscope bulb with a closed stopcock, wash with alcohol to prevent the clouding of the window, fill it with gelatin solution and place in an ice-chest for 24 hours. The ultramicroscopic image first shows a considerably increased illumination of the whole light cone; later, a great number of light rays appear, which orient themselves to form a coarse structure in an apparently regular manner.

¹ At higher temperatures the sealing wax which binds the cover-glasses to the cuvette melts.

For a control experiment,¹ liquefy the gel by moistening the bulb with water at 40°–50° C. for a few minutes. Observe the considerable decrease in the intensity of the light cone, the disappearance of the Brownian movement. These effects may also be observed when the gelatin solution is heated to a higher temperature in order to completely disintegrate the coarse aggregates formed by gelation. By studying the process of gelation with a strong lighting apparatus, one may observe the gradual transitions from Brownian movement to oscillatory motion to complete immobility of the particles, and finally, to the formation of larger aggregates (W. Menz, W. Bachmann).

Expt. 88. Ultramicroscopy of the ageing of starch pastes—Ultramicroscopic observations may be made together with viscosimetric experiments on the ageing of a 1 per cent. starch paste (Expt. 75) so as to co-ordinate changes in turbidity with the variations in its viscosity. The presence of particles possessing Brownian movement is especially evident with the occurrence of complexes in aged starch sols. Brownian movement is absent or only very slight in cold freshly prepared starch pastes.

Expt. 89. Ultramicroscopy during coalescence—Fill the ultramicroscope with a very dilute mastic hydrosol or black India ink. Copy the image and count the number of particles in a portion of the field bounded by an ocular grating. Use the centre of the optical field for the observations. Add to the bulb about two drops of HCl or BaCl₂ and thoroughly mix the contents by pouring the whole solution into a small beaker and back again into the bulb. After standing a few minutes there is a decrease in the Brownian movement with the formation of larger

¹ The cuvette should be carefully washed after these experiments by means of tepid warm solutions of KI, KCN or KCNS, which are good solvents of gelatin.

irregular aggregates. Another count shows a decrease in the total number of particles as a result of aggregation. Similar experiments with red gold sols show a change of colour when the particles aggregate and hence decrease in number (Expt. 60). The coagulation of dilute ferric hydroxide sols with a drop of NaOH is striking. Slightly disperse granular particles are seen to coalesce in groups which become quite distinct from one another and finally unite to form very large flakes. A similar coagulation process may be observed by flocculating 0.01 per cent. sols of Congo rubin and antimony sulphide (Expt. 13).

ROTATION OF THE PLANE OF POLARIZED LIGHT BY COLLOIDS

Hydrated colloids such as egg white, gelatin, tannin, starch paste, etc., strongly rotate the plane of polarized light. This phenomenon is very interesting and yet has been little investigated. An ordinary saccharimeter with a sodium flame, intensely illuminated to overcome the turbidity of the solution, is suitable for observing this phenomenon.

Expt 90. **Optical rotation by gelatin solutions** (H. Trunkel)—The degree of optical rotation of a gelatin solution is as variable a property as its viscosity. The degree of rotation increases with increasing concentration, decreasing temperature and is also dependent upon the age of the gelatin solution. The effect of age upon optical rotation may be determined as follows: Fill a 200 mm. polarimeter tube with a freshly prepared gelatin solution of a concentration such that the intensity of the light source may suffice. The experiment should be performed at constant temperature especially if the polarimeter is provided with a water-jacket. Record the degrees of optical rotation every hour and observe the constant

increase at high concentrations and low temperatures. The degree of rotation generally reaches a maximum after 2-4 days.

The following results were obtained at room temperature by using a clear 5 per cent. solution of gelatin, a 200 mm. polarimeter tube and sodium flame:—

<i>t</i> Time in Hours.	α Rotation.		Δ in per cent.
	Observed Degree.	Calculated Degree.	
0.47	7.67	7.67	0.0
0.72	7.94	7.94	0.0
2.48	9.72	7.49	+ 0.23
3.72	10.15	10.09	+ 0.06
4.47	10.27	10.42	- 0.13
5.55	10.63	10.79	- 0.16

The calculations conform to the equation $\alpha = Kt^n$, in which t is the time and K and n are constants.

Expt. 91. **Optical properties of vanadium pentoxide sols** (H. Diesselhorst and H. Freundlich)—The freshly prepared sol, Expt. 33, does not appear to have optical properties. A vanadium pentoxide sol, after standing a few weeks, when stirred with a glass rod, shows silky streaks. These streaks are yellow in reflected light and dark in transmitted light. The sol, which can be diluted to give a bright brown colour in transmitted light, is placed in a cuvette between two crossed Nicol prisms. On stirring, a brightening of the field of vision is observed, after which dark clouds reappear. A sol kept for six months is so sensitive that it glows on slight stirring. This is the characteristic behaviour of a fluid crystal.

COLOUR OF COLLOID SOLUTIONS

The colour phenomena in colloid solutions are brought about in two ways. Colloid particles show a selective absorption of light rays possessing certain wave-lengths. Some of the colour phenomena are due to the small size of the particle, which radiates laterally a considerable amount of light. This type of radiation is selective and hence various colloids reflect different coloured light rays. These conditions of colloidal state account for the double colour phenomena often occurring in colloids, wherein the difference in colour depends whether the light is transmitted or reflected. Selective adsorption no doubt gives the colour to transmitted light, while selective radiation is responsible for the colour of reflected light. Often, the colour of the reflected light is complementary to the colour of the transmitted light.

Selective adsorption and selective radiation, together with the degree of dispersion, the orientation as well as the shape and mass of the particles play a considerable rôle in the colour change.

COLOUR OF "COLOURLESS COLLOIDS"

Colourless substances are those which absorb ultra-red or ultra-violet light rays. If these substances are dispersed in colourless dispersion media, they show the usual colour phenomenon of opalescence irrespective of their individual properties. These sols impart a yellow or red colour to reflected light. The best example of such an opalescence is the cloudy sky at sunrise and sunset due to transmitted light and in the daylight due to light reflected from a dark background. This opalescence results from the retardation of the light of shorter wave-lengths by the colloid particles, that is, they retard the

blue and violet rays more than the longer yellow and red rays. The yellow and red light rays pass through the colloid with the least amount of retardation by the particles, while the blue and violet rays are strongly refracted or radiated. Thus, light is dispersed into its different wave-lengths so that the longer waves passing through produce absorption colours, while the shorter waves are deflected laterally, producing refraction colours. Opalescence may be distinguished from fluorescence by the fact that opalescent light is, while fluorescent light is not, polarized (Expt. 78).

Expt. 92. **Opalescent solutions**—A beautiful opalescent solution may be prepared in the following way: Pour about 50 c.c. of a 0.1 per cent. alcoholic solution of mastic or colophonium into 200–300 c.c. of distilled water or prepare a sulphur sol according to Expt. 11.

Add in small portions 100–200 c.c. of boiling distilled water to about 50 c.c. of a 0.5–1.0 per cent. filtered solution of dried egg albumin preserved in a 0.9 per cent. NaCl solution. To prepare a sol of fresh egg white, as in Expt. 103, beat the white to a foam and allow to stand. Separate the clear fluid from the membranous foam. Dilute this clear liquid with four times its volume of 0.9 per cent. NaCl solution and slowly add 300 c.c. of boiling water.

Other beautiful colour phenomena obtained from colourless dispersoids are the so-called Christiansen diffraction colours observed in the NaCl gel prepared in Expt. 27. Furthermore, polymerized cinnamic acid ethyl esters; many liquid crystals; fine suspensions of glass, quartz, NaCl etc., in mixtures of organic solvents, which have almost the same coefficient of refraction, also show these colour phenomena. See B. C. Christiansen, *Ann. d. Physik.* **23**, 298 (1884); **24**, 439 (1885). A simple example of this phenomena is an aqueous saturated

solution of H_2S , in which decomposition has begun. By holding the coalescing solution against the light, a distinct violet absorption colour may be observed. $NaCl$ gel produces the two colours, yellow and bluish green; and cinnamic ester the colours green and red at room temperature, and yellow and blue at higher temperatures.

COLOURS OF COLLOIDAL METALS

Colloid metals show a great variation in colour phenomena. M. Faraday pointed out that the degree of dispersion is largely responsible for colour formation.

Expt. 93. **Polychromism of gold sols**—Expts. 2–7 give the methods of preparation of red, violet, blue and green gold sols. A simple experiment which successively produces all the gold sol colours mentioned is similar to the method described in Expt. 3, using alcohol and a reducing agent. Use a large volume, 100–150 c.c. of boiling water, and add in the manner described above, 5–10 c.c. of a 0.01 per cent. gold salt solution, and the same amount of alcohol. Warm the mixture until the red colour is developed. Pour a test portion of the hot sol into a small Erlenmeyer. Keep the main portion boiling continually and add, drop by drop, more gold salt solution, without any addition of alcohol. Continue to heat until a violet to blue sol appears and remove another test portion. To prepare a green sol, add 10–20 c.c. more gold salt solution to the remaining 50–100 c.c. of hot violet sol. Observe that in such a series of variously coloured gold sols, prepared from the same original solution, the increase in turbidity follows the order of colour change from red to green.

Expt. 94. **Polychromism of silver sols**—A series of coloured silver sols ranging from bright yellow, through the various shadings of red to blue and bluish black,

is prepared in the following manner: First prepare three solutions: 0.01N AgNO_3 , 0.001M hydroquinone [$\text{C}_6\text{H}_4(\text{OH})_2$] and 0.01N sodium citrate. Make the latter solution by titrating 0.5N citric acid with an equal volume of 0.5N NaOH until added phenolphthalein just assumes a pink tinge. All solutions, especially the AgNO_3 , should be neutral. Use freshly prepared hydroquinone solution. A very slight excess of alkali is necessary for reduction. Make the following preliminary experiments in order to standardize the hydroquinone solution. Add 2 c.c. of hydroquinone and 4 c.c. of sodium citrate to 2 c.c. of silver nitrate solution. If the mixture does not develop a faint yellow colour after 10 seconds, add a drop of dilute NH_4OH to 100 c.c. of the sodium citrate solution and repeat the experiment. Should the yellow colour not appear in 10 to 15 seconds, add two drops of NH_4OH to the citrate solution and continue to do so until the desired reaction takes place. The presence of much NH_4OH soon destroys the coloration by flocculating the silver sol.

After standardization of the citrate solution, place 2 c.c. of the AgNO_3 solution into ten well-cleaned test-tubes, and add the following mixtures of hydroquinone and sodium citrate.

Exp. No.	1	2	3	4	5	6	7	8	9	10
Hydroquinone	5 drops.	7 drops.	10 drops.	14 drops.	1 c.c.	1.4 c.c.	2 c.c.	2.8 c.c.	4 c.c.	5.6 c.c.
Citrate .	16 c.c.	11 c.c.	8 c.c.	5.6 c.c.	4 c.c.	2.8 c.c.	2 c.c.	1.4 c.c.	1 c.c.	14 drops

If no reaction is evident in the first two or three tubes, a few more drops of NH_4OH may be added to them without danger of flocculation. All the mixtures first assume a yellow or red colour, but they gradually develop a graded series of colours toward the blue of the last tube. After

3 hours, the tubes have the following colours: 1, bright yellow; 2, yellow; 3, orange-yellow; 4, orange; 5, red-orange; 6, red; 7, red-violet; 8, violet; 9, blue-violet; 10, blue. The last sol must be diluted with water in order to make the colour more distinct. The sols remain stable a few days, when all the colours gradually change to blue.

Green sols cannot be prepared in the cold by this method. Pour the above mixtures all together, stir and heat to boiling. A yellow sol appears before the colours fade. If solution 10, which finally becomes blue, is heated at the point where it is faintly red, a greenish coloured sol forms. Continued heating produces a yellow sol and finally changes it to a blue one. By this method, approximately any shade of green between blue and yellow may be prepared.

Observe the increase in turbidity in the series ranging from yellow to blue. The continuous change in colour from yellow to blue corresponds to a change in the absorption maximum of the shorter to longer wave-lengths with a decreasing degree of dispersion. This is a general phenomenon in colloid chemistry illustrating the relation between colour and degree of dispersion.

Expt. 95. **Polychromism of sulphur sols** (R. Auerbach)—Mix 10 c.c. of 1.33 per cent. phosphoric acid (10 c.c. of commercial H_3PO_4 and dilute to 150 c.c.) with 10 c.c. of 0.05 m. $\text{Na}_2\text{S}_2\text{O}_3$. After a few minutes, the absorption colour becomes yellow; reflected colour, blue; then the absorption colour becomes red; the reflected colour very turbid and greyish white. Later a dark blue or occasionally green shade appears, and finally flocculates to give a white, coarsely disperse sulphur sol.

Expt. 96. **Colour changes in gold sols during flocculation**—The relation between colours of sols and

the size of their particles is evident by the sudden change of red gold sol into a violet or blue upon addition of an electrolyte which produces flocculation.

Place in large test-tubes or Erlenmeyer flasks equal volumes of a red gold sol and add to respective portions a drop of dilute HCl, NaCl, BaCl₂, etc. After a few seconds, the red sol suddenly changes into a violet or blue sol. The occurrence of turbidity in the Tyndall cone, the ultramicroscopic image and the ultimate appearance of flocculation show that the gold sol forms greater complexes during the sudden colour transition. Reversible colour changes of colloidal gold in the presence of casein have been shown by R. Zsigmondy, *Nachr. d. Göttinger Ges. d. Wiss.*, January, 1916.

The silver sol prepared in Expt. 94 shows the sudden change of colour upon flocculation with electrolytes. The colour of the silver sol after complete flocculation is usually black.

Expt. 97. **Colour changes in Congo-rubin sols**—The particles of this dye sol have diameters between those of colloids and molecular dispersoids. It may be suddenly transformed to a blue-violet or blue solution not only upon addition of acid but also by the addition of any neutral salt or even alkaline substances. The dye behaves like a red gold sol in many respects and it may be used as a gold sol substitute. The colour transition of Congo rubin is reversible by dilution, by raising the temperature, by addition of alcohol, etc. The colloidal changes in this dye are observed in the following experiment:

Use a 0.01 per cent. solution of Congo rubin. Place 10–20 c.c. of Congo-rubin solution in a large number of test-tubes and add to respective tubes a few drops of some common chemical reagents. All electrolytes cause colour transition except strong alkalies and NH₄OH.

Warm the Congo-rubin solution, coloured blue-violet by a small amount of electrolyte, until the solution turns red. Pour half of this hot solution into a cold test-tube and cool further in a stream of water. The red solution turns blue once more.

To a large beaker of distilled water add, drop by drop with constant stirring, a solution of Congo-rubin blue dye. After a few minutes the violet tinged solution changes to bright red.

Add 2-3 c.c. of a blue Congo-rubin solution to an equal volume of methyl or ethyl alcohol. The red colour again appears with a simultaneous disappearance of turbidity.

For further experiments with Congo rubin, see numbers 159, 177 and 179.

Expt. 98. **Colour and degree of dispersion**—From the preceding experiments, the relations between colour and degree of dispersion of variously coloured gold, silver and Congo-rubin sols have been illustrated. This relation is important especially in the theory of colours of substances in the colloid state. The following experiments demonstrate this relation:

Ultrafilter according to Expt. 57, red, blue, green gold sols, yellow, red and blue silver sols, red and blue rubin solutions. The first members of these series pass unchanged through the 2-4 per cent. collodion filter. However, the ultrafilter retains the blue and green sols, while the behaviour of the intermediate series varies.

A mixed colour sol is changed by ultrafiltration, so that a sol of another and purer colour constitutes the ultrafiltrate. Add a few drops of dilute acid or neutral salt, baryta, etc., to a Congo-rubin solution, so that a violet shade just appears, and ultrafilter this solution. The filtrate consists of the red coloured sol. Pour together the different coloured silver sols obtained in Expt. 94 and ultrafilter the mixture. A highly disperse

yellow silver sol is obtained as an ultrafiltrate from the dark grey mixture.

The relation between colour tone, turbidity, and ultramicroscopic images of colloids was brought out in the above experiments. Compare the ultra-image of the red Congo-rubin solution, and the image of the blue solution, upon addition of electrolytes.

Expt. 99. **Ultramicroscopic colours**—The colour of the particles visible in an ultramicroscope is due to the selective absorption, selective refraction and radiation. Lateral radiation colours of colloid particles may be observed microscopically in very dilute solutions. When using large quantities of concentrated solution, the colloid layer lying above the light cone acts as a light filter. The radiated colours of the single particles are altered by the absorption colours of the entire colloid.

Concentrated ferric hydroxide sol studied under the ultramicroscope gives an intense brownish-yellow cone. If the same solution is diluted, the colour cone becomes greenish white. Likewise, a very concentrated red gold sol often gives a brown Tyndall cone and upon dilution a pure green. Concentrated Prussian blue sols show a violet cone and upon dilution give a brownish-yellow cone.

The ultra-colours of colloid particles are often complimentary to their absorption colours provided very dilute solutions are compared with one another. Red gold sols usually give a green, blue or brown-yellow Tyndall cone.

Polychrome ultra-images are often obtained when sols are examined under an ultramicroscope. A green-grey silver sol prepared by mixing coloured sols, has a wide range of particle size which gives a number of radiation colours. Complex reflection colours due to coarser microscopic particles may also be observed. Another

example is given by brownish-red, commercial colloidal selenium. A polydisperse system contains particles of various sizes which give a grey colour to the solution due to their individual absorption colours, when viewed by the naked eye. Ultramicroscopic inspection of this sol shows the individual colours. These phenomena indicate a close relationship between the colour of a sol and its degree of dispersion.

ELECTRICAL PROPERTIES

MOST colloid particles migrate when an electric current is passed through their sols (Electrophoresis). This indicates that the particles possess electric charges. From the capacity of transporting electricity it follows at the same time that colloid solutions must have a conductivity of their own, apart from the conductivity of the dispersion medium and the ordinary electrolytes contained in it. Typical colloid particles generally possess a relatively large number of unit charges, 30 to 40 in contrast to the ions of ordinary electrolytes (acids, bases and salts). Moreover, the charge on colloid particles can be both positive or negative. Therefore, colloidal gold and ferric hydroxide may occur as either anions or cations. Such is not the rule in molecular disperse solutions.¹ The changes in conductivity with concentration, temperature, etc., partially follow laws different from those applicable to molecular disperse electrolytes. Transitions of "colloid electrolytes" (McBain) to "molecular electrolytes" may occur as in the case of ferric hydroxide sols, according to W. Pauli and J. Matula. The term "ion" which has been applied to electrically charged particles in gases must be used,

¹ The exceptions are so-called "amphoteric electrolytes," as hydrolytic products of proteins (leucine, alanine, etc.), alkaloids, caffeine, theobromine, etc.

therefore, in a broader sense to include electrical charged colloid particles.

The methods of studying the electrical charges of colloid particles may be arranged in the three following groups :

U-tube method—The simplest apparatus for the detection of the sign of the charge on colloid particles consists of an U-shaped glass tube. The tube is 15 to 20 cm. high and has an inside diameter of 2 to 3 cm. Two pieces of platinum or silver wire, which are twisted into an horizontal spiral, serve as electrodes. These are stuck through two cork stoppers. Bore a hole in each stopper or cut a groove along the side so

that any gases which are formed may escape. Fill the tube with the colloid to be studied and pass a 110-volt direct current from the main through the solution. If the colloid is coloured, electrophoresis may be detected by a gradual disappearance of colour from one side of the tube after 15 minutes. The sign of the charge on the particle may also be deduced from this phenomenon. If the

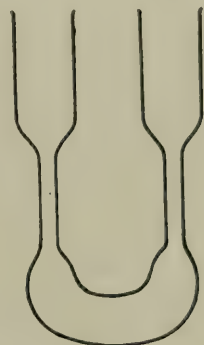


FIG. 8.

colloid is colourless, pass the current through it for 30 minutes. Shut off the current, remove the stoppers without disturbing the liquid and pipette off the uppermost 10–20 c.c. of liquid in each side of the tube. Determine the concentration of the colloid in each portion of the liquid by the methods previously given.

Accurate studies on the rates of electrophoresis may be made if polarization and electrolysis are eliminated at the electrodes. Polarization may be overcome if an U-tube is used which has a constriction in the middle of both arms (Fig. 8).¹ Fill the lower bulb with colloidal solution to the upper ends of both capillaries. Prepare

¹ U-tubes of this form have first been devised by J. Billitzer.

two small plugs of filter paper and place one in each capillary so that the tubes are stoppered. Invert the U-tube and wash out the upper parts of the arms with distilled water. Fill the rest of the tube with distilled water to serve as an electrode fluid. Since distilled water has a low conductivity, quite a length of time may elapse before considerable electrophoresis has taken place. A very dilute electrolyte makes a suitable electrode solution. If possible, such an electrolyte should be chosen which exists in small amounts in the colloid to be studied.

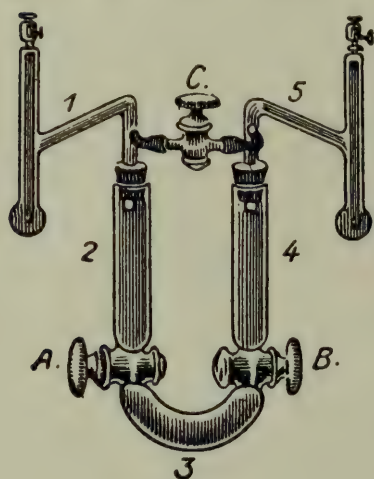


FIG. 9.

Use a dilute solution of KI or AgNO_3 in the experiments on silver iodide sols, and in the study of ferric hydroxide sols, use a dilute solution of FeCl_3 . The best method is to use the ultrafiltrate of the colloid studied, for the electrode fluid. The ultrafiltrate may be obtained in sufficient amounts by simple ultrafiltration. It is not necessary that the electrode fluid touch the stoppers when they are in place. Maintain the fluid in both arms at the same level. Carefully remove the paper plugs with tweezers. If this is done correctly, a sharp surface boundary remains in the constriction of the arm. A tube of the dimensions given requires a current of 80 to 110 volts.

Use the conversion apparatus given in Fig. 9 for more accurate studies.

The middle part, 3, is filled with the colloid to be studied, until the liquid rises slightly above the stopcocks A and B. Close A and B and wash the cathode and anode arms 2 and 4. Fill the arm tubes with a conducting liquid

whose concentration is the same as that of the colloid studied, in order to obviate diffusion potentials. Add the attachments 1 and 5, leaving the tap C open, and fill them with the same conducting liquid by means of a 10 c.c. pipette. After removing all air bubbles, place the apparatus in a support and close stop-cock C.

Add about 0.2 g. of CuCl_2 to the cathode solution and about 1 g. of NaCl to the anode solution so as to prevent polarization. Thoroughly mix the NaCl and the anode solution by moving the silver electrode to and fro. Use a plated copper foil or wire for the cathode and coat all but the lower end with paraffin. This precaution allows the current to enter the solution at points where the cathode is in contact with the dissolved copper salt. Before passing the current, open tap C, until the level of the fluids in both tubes is the same, then close again. Open A and B and observe, every few minutes, whether a displacement of the middle layer occurs without the flow of current. If such does not occur, the current may be started.

Ultramicroscopic methods for investigation of electrophoresis—Measurements of the electrophoretic rate of displacement of individual particles are made by means of the ultramicroscope. Construct a small glass chamber on the object support of the microscope according to the process of The. Svedberg. Place two small pieces of glass on the right and left sides of the object support and two rectangular cover-glasses at the front and back. Seal all joints. A current of 4 to 6 volts is led into the chamber by two thin platinum or silver foils fastened on the right and left sides and connected to the conducting wires by pinch contacts. The chamber is finally closed with a cover-glass. Illumination from the front is furnished by an ultramicroscope. These experiments are

described by Svedberg and Anderson in *Koll. Zeitschr.*, **24**, 156 (1919).

This method eliminates disturbing influences of the walls of the vessel. The electrophoretic rate of movement of the single particles may be observed and measured by means of a specially prepared microscopic bulb. Draw out a piece of glass tube about 1–5 cm. in diameter, so that the diameter of the constricted part is about equal to that of the bulb outlet. Bend the narrow part of the tube at right angles and cut off the larger end so that its upper end is level with the top of funnel attached to the bulb. Tightly fasten this tube to the bulb outlet with a short piece of rubber tubing and bind with wire to hold it in a perpendicular position. The bulb now has a funnel at both ends. Carefully introduce flexible 0.5 mm. platinum or silver wires into the bulb through each of the two openings. The ends should be in the same plane and 0.5–1.0 cm. from each other. Use a current no greater than 10 volts.¹ Obviate overheating by passing the current through the sol by means of a pinch contact and only for short periods of time. Electrophoresis is manifest by the particles, capable of Brownian movement, continually moving in one direction through the influence of the electric current. Try the experiment with a mastic sol prepared in Expt. 1. Its particles are always charged negatively. Observe the direction of migration of the particles in the ultramicroscope. Measure the relative rates of certain particles passing over a given area, taking the time with a stop-watch. Other portions of the colloid solution may be studied by tipping the cuvette back and forth. This tipping will also mix the

¹ The nearer the electrodes are to each other, the smaller the voltages necessary. Conversely, the effect may be increased with a given small voltage by carefully approximating the electrodes.

products of electrolytic dissociation and render them harmless.

The velocities of electrophoretic moving particles are calculated from the following formula :

$$c = \frac{s}{t} = b \frac{P}{d},$$

where s is the distance in centimetres covered in t seconds, P the potential difference in volts, d the distance in cm. between the electrodes, b a constant characteristic for each sol, which may be defined as the electrophoretic mobility of the colloid particles studied. Experimentally

$$b = \frac{s d}{t P}.$$

Its value usually lies between 1 and $10 \times 10^{-3} \frac{\text{cm. cm.}}{\text{sec. volt}}$ and is approximately of the same magnitude as the mobility of ordinary ions.

Capillary method for the study of electrophoresis

—This method involves the characteristic behaviour of certain colloidal solutions to rise by capillarity in filter paper and will be described in Expt. 105.

Galvanic couples (W. Biltz)—Make a galvanic couple by soldering the ends of a strip of zinc 7 cm. long and 1 cm. wide to the end of a copper strip of the same size and bend both strips at right angles to the soldered joint. Dip the ends of the galvanic element into the sol to be studied. The suspensoid sol flocculates in a short time, the positively charged particles adhere to the copper strip or remain in its vicinity, while the negative particles adhere to the zinc strip. In strongly hydrated systems, such as egg-white solutions, the electrophoresis requires a longer time, but ultimately gives the same results.

The sign and magnitude of the electrical charges in colloidal solutions are extremely unstable and vary to a considerable extent. Investigations show that colloid particles bearing positive and negative charges, may occur in the same colloid solution. This will be demonstrated in the following electrophoretic experiments. Indefinite results are sometimes obtained due to the great variability of the electrical properties of the colloidal particles rather than to the method used.

Expt. 100. **Positive and negative colloids**—Study the electrophoresis of 0.25 per cent. ferric hydroxide sol, prepared in Expts. 20–22 by the U-tube method. Dialysis of the sol may be performed in a parchment paper cup. Use parallel connections and perform the same experiment with mastic hydrosol (Expt. 1). A considerable repulsion of the ferric hydroxide colloid by the anode, occurs after 10 to 15 minutes and the particles gather at the cathode. The ferric hydroxide sol is therefore positively charged. Conversely, there is a repulsion of mastic sol by the cathode. The colloid is therefore negatively charged.

Test with the galvanic couple described above, the type of electric charge on As_2S_3 and $\text{Fe}(\text{OH})_3$ sols prepared in Expts. 12, 20–22. Examine the precipitate removed from the inside of both arms of the couple with filter paper. The sulphide has migrated to the zinc strip and the hydroxide to the copper strip.

Observe that with a short galvanic element, all positively charged particles, ions as well as colloids, migrate to the nobler metal, in this case, copper. If such an element is used as a source of current for an electrophoresis experiment in an U-tube, the motion of particles would occur as described in Fig. 10. Connect the platinum electrode with the zinc strip for a cathode and with the copper for an anode. The positive $\text{Fe}(\text{OH})_3$

sol will migrate from the anode to the cathode. Colloidal hydroxides often possess positive charges; colloidal metals and sulphides, negative charges.

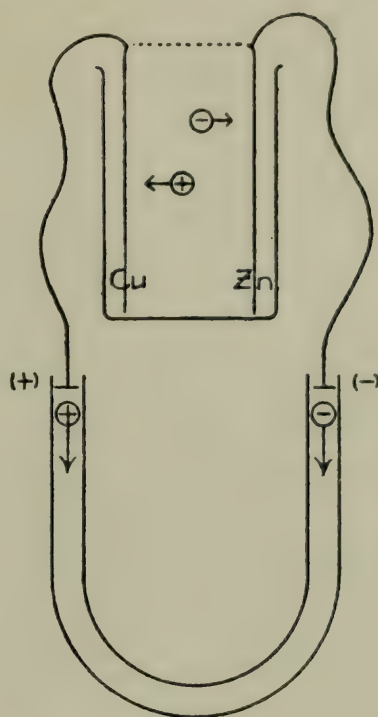
Expt. 101. Changing the sign of the charge on colloid particles by varying the mode of preparation—Prepare two silver iodide or silver bromide sols in the following manner:

Sol A. Dilute 3 c.c. 0.1N, KI, or KBr with 10 c.c. H_2O . In a second vessel dilute 5 c.c. of 0.1N $AgNO_3$ with 40 c.c. of H_2O . With strong agitation, slowly pour the KI solution into the $AgNO_3$ solution, and not in the reverse order.

Sol B. Dilute 4 c.c. of 0.1N $AgNO_3$ with 15 c.c. of H_2O . In another vessel, dilute 5 c.c. of 0.1N KI with 40 c.c. of H_2O . Pour the aqueous $AgNO_3$ into the KI solution.

Sol A is found to be positively, and sol B negatively charged when the electrophoresis is studied with an ultramicroscope.

Theory states that the common ion, present in an excess when the colloid is formed, imparts its charge to the colloid particles. If the $AgNO_3$ is poured into the KI, the negative anion, I^- , is first present in excess and



⊕ positive Colloid
⊖ negative "

FIG. 10.

it imparts its negative charge to the AgI sol. If the KI is poured into the AgNO₃, the positively charged cation Ag⁺ is first present in excess and it imparts a positive charge to the AgI sol.

Expt. 102. **Positive and negative ferric hydroxide sols**—The commercial ferric hydroxide sols and those prepared in Expt. 21 are positively charged according to electrophoresis experiments, that is, U-tube method. Negatively charged ferric hydroxide sols may be prepared in the following way: Add, drop by drop, a saturated solution of FeCl₃ to 100 c.c. of 2N ammonium carbonate, shake continually until the precipitate first formed has dissolved to give a dark reddish-brown, clear fluid. If the solution begins to darken, wait a few minutes, so as not to add an excess of FeCl₃. This colloid eventually loses its electrical charge upon dialysis. Determine the sign of the charge on the colloid particles in an undialysed sol by capillary, U-tube method, etc.

Pour 100 c.c. of 0.01N FeCl₃ solution into 150 c.c. of 0.01N NaOH solution. A bright yellow opalescent sol appears which seems to be less hydrolysed than the usual ferric hydroxide sols. It may be examined with an ultramicroscope.

Expt. 103. **Influence of (H⁺) and (OH⁻) ions on the sign of the electrical charge on egg-white suspensoid particles** (W. B. Hardy)—Prepare as in Expt. 92, a sol of fresh egg white coagulated by heat. Allow it to stand a few days so that it may better tolerate the addition of acid. This sol reacts neutral toward litmus paper, and when examined by the U-tube method, a weak negative charge is sometimes observed. Acidify a small portion with acetic acid so that litmus paper shows a distinct acid reaction. Make another portion alkaline with NaOH. Perform a double experiment with these sols in two U-tubes or in two Michaelis

apparatus. The acidified sol shows a decided cation migration and hence it is positively charged. Conversely, the alkaline sol shows a distinct anion migration hence, negatively charged. These sols are suitable for an ultramicroscopic study of electrophoresis.

Expt. 104. **Changes in the electric charges of ferric hydroxide sols by filtration** (T. Malarski)—Filter a dilute, dialysed commercial ferric hydroxide sol five times. Use a fresh filter paper each time and add to it some shreds of filter paper in order to increase its effect. Study the electrophoresis of unfiltered and filter sols simultaneously, using parallel connections. The unfiltered sol shows a sharply defined clear portion in the vicinity of the anode arm; the filtered sol shows none or only a diffuse brightening. The unfiltered solution gives a thick dark-brown precipitate; while the filtered sol gives an extremely voluminous bluish-white precipitate in the cathode arm.

According to T. Malarski, *Koll. Zeitschr.*, 23, 113 (1918), filtration of positive sols through negatively charged filter paper should first decrease the amount of positive electricity in the sol and finally charge it negatively. The effect of the filter paper on the electric charge of the sol may be accentuated by repeated filterings.

Expt. 105. **Detection of electrically charged colloid particles through capillarity** (F. Fichtner, N. Sahlbom)—Allow some coloured hydrosols to ascend strips of filter paper. Different properties are observed depending upon the charge of the sol. Metals and sulphide sols show a considerable separation between disperse phase and dispersion medium in the rising portion of the sol. Ferric hydroxide sols prepared in Expt. 21 show a distinct separation of both phases after a short rise. The colourless dispersion medium continues to ascend while the dispersed phase remains behind,

becomes concentrated and flocculates to form a sharp boundary. Fichtner and Sahlbom claim a negatively charged colloid will ascend the strip of filter paper unseparated from its dispersion medium, while the positively charged colloid is separated. The explanation of these various properties of colloids lies probably in the assumption that the filter paper wetted by the water carries a negative charge. While a negatively charged capillary adsorbs a similarly charged colloid particle unaffected, the oppositely charged particles are held back and collected so that they finally clog the capillary.

Examine by capillarity a commercial ferric hydroxide sol and one prepared in Expt. 94. The former, positively charged, ascends only 1-2 cc. and flocculates, giving a sharp irregular-shaped border line; the negative sol ascends almost unseparated and at nearly the same rate as the dispersion medium.

Examine by capillarity a 0.2 per cent. solution of "night blue" and a 0.2 per cent. solution of "alkali blue." Distinct differences are obtained if a concentrated "alkali blue" solution is compared with the dilute "night blue" solution. Addition of NaOH to "alkali blue" and HCl to "night blue" emphasizes the differences between the properties of the two dyes. While the "alkali blue" ascends readily and therefore appears negative, the "night blue" rises a short distance and precipitates. Therefore it appears to be positively charged.

These differences may be detected more quickly by dropping some hydrosol on to a filter paper. Examine the two ferric hydroxide sols by this method. After the drops have spread, hold the filter paper against a light. A positive sol forms a broad colourless ring surrounding a coloured centre portion. A negative sol gives a spot which is uniformly coloured to the outer edge.

Expt. 106. **Capillarity with prepared filter paper**—Soak some filter paper with $\text{Al}(\text{OH})_3$ sol, prepared in Expt. 32, and allow to dry in a warm place. Study the capillarity of this prepared paper. The $\text{Al}(\text{OH})_3$ sol is no longer positively charged. Therefore, the “night blue” solution separates upon absorption, while the “alkali blue” flocculates at the line of contact between the paper and liquid.

The sign and magnitude of the electric charge on colloid particles are characteristics which are more stable than the degree of dispersion of the colloidal suspension. However, simple filtration through a filter paper (Expt. 104) may suffice to change these properties.

The capillary method may be used with care for the detection of the kind of charge on colloid particles.

VI

EXPERIMENTS WITH GELS

GELS are disperse systems which show both solid and liquid properties. As solid bodies, they possess a relative stability in shape and elasticity, especially toward rapid changes in form. However, they behave as fluids toward continued mechanical stress. They gradually assume the shape of any new container due to stress caused by their own weight. Diffusion of molecular disperse substances in dilute gels proceeds practically with the same velocity as diffusion in a pure dispersion medium.

Expt. 107. **Mechanical properties of pastes**—The changing liquid and solid properties of pastes may be used to conveniently demonstrate the properties of real gels. Grind 5 g. of potato starch in a mortar with 4 c.c. of water. Tip the mortar and allow the paste to flow in a continuous stream on to a glass plate. Smaller amounts give the drop form characteristic for liquids. Quickly rub the paste in a mortar with a spatula. The paste breaks into shell-shaped fragments showing sharp fracture surfaces. Therefore the paste behaves like a liquid by slowly altering its surface and behaves as a solid when a relatively large stress is applied.

Gels are formed as a result of change in the following properties of a colloid system: (1) concentration, (2) temperature, (3) degree of hydration usually attended by chemical changes, (4) formation of insoluble precipitates.

Many gels having great elasticity and temporary rigidity, such as gelatins, may be classed as liquid-liquid systems. There are probably gels having the structure liquid-solid and solid-liquid. Silicic acid gels show emulsoid properties in the first stages of formation and on ageing they show a suspensoid structure. This structure corresponds to the changes of elasticity with the age and to the first occurrence of crystalline Lauegrams in the aged jelly.

A. GELATION

Gelation includes the formation of a hydrated emulsoid, reversed by heating. Externally, the process of gelation corresponds to a large increase in the viscosity of the liquid sol and associated with the properties of solid substances such as displacement, elasticity, rigidity of form, etc. The process of gelation may be expressed in the following terms: (1) Time of gelation. Concentration and temperature being constant, the gel formation, similar to all colloidal changes of state, requires a certain time. (2) Gelation concentration at a certain time and temperature. Jelly formation occurs only above a certain concentration. (3) Solidifying temperature. Time and concentration being constant, jelly formation occurs only below a certain temperature. A fourth stipulation may include the softening temperature of gels, which is usually higher than the solidifying temperature. Therefore, these softening temperatures do not coincide with the melting and freezing temperatures of crystalline substances.

Viscosimetry of dilute gelled solutions is a convenient method for studying the process of gelation. The properties of concentrated solutions may be extrapolated from these results with considerable accuracy. The properties of a gel may be defined in terms of the condi-

tions under which it exists—concentration, temperature, time, etc.,—at which the colloid will no longer flow from the container when it is inverted.

Expt. 108. **Determination of gelation concentration and time**—Prepare in the manner described in the chapter preceding Expt. 66 a 12 per cent. gelatin solution and dilute it with warm water so as to give solutions of 12, 8, 6, 4, 3, 2, 1.5 and 1.0 per cent. Pour 10 c.c. of each solution in a test-tube, and place a thermometer in the test-tube containing the 4 per cent. solution. Quickly cool all the tubes to room temperature or to 10° with cold water.¹ By carefully inclining the tubes held in a test-tube rack, determine the time elapsed before the gel in each tube ceases to flow. This experiment furnishes a series of periods of gelations at various concentrations. Plot a time-concentration curve. The plotted curve may be used to interpolate the gelation concentration which gives a gel at room temperature in less than an hour. Repeat the same experiments by warming the gels on a water-bath or a hot plate. Plot the corresponding time-concentration curve of gelation at constant temperature and by interpolation find the concentration of the solution which will give a gel in an hour.

The “normal” gelation concentration, that is, the concentration at which a solution solidifies within half an hour, depends upon the mode of preparation. The concentration of the solution is approximately 2 per cent. at 15° C. and usually nearer 1 per cent. at 0° C.

Perform the same experiments with agar, soap solution and caproic acid. Agar is a carbohydrate and unlike gelatin contains no albumin. The normal gelatin concentration of agar is usually less than that of gelatin.

Expt. 109. **Determination of solidifying and soften-**

¹More accurate results are of course obtained by use of a thermostat.

ing temperatures—The temperature at which a gelling solution solidifies or melts depends essentially upon the rate of temperature change. The slower a gel is cooled, the higher the temperature at which it solidifies. The slower a gel is warmed, the lower the temperature at which it melts. A constant rate of temperature change, such as 1° C. per minute, must be used in order to obtain comparable results. A cooling rate of 40° to 30° C. in 10 minutes might be called the normal rate, while cooling in 50 minutes would be a 0.2 normal rate of temperature change. This rate of temperature change, 1° C. in 5 minutes, is especially desirable for the following experiments:

Use thin-walled test-tubes of equal size or if possible, metal test-tubes. Provide a water-bath (glass tank of 2 to 3 litres capacity) with stirrer and fill the tank with water at about 40° C. Punch holes of such a size in a piece of stiff paper or sheet metal so that it rigidly holds the test-tubes. Place the perforated sheet above the water-bath. Liquefy

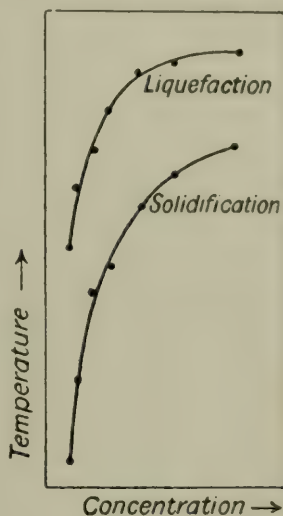


FIG. II.

the series of eight gelatin solutions used in the previous experiment by placing them all in the water-bath heated to 60° or 70° C. Leave the tubes in the bath and allow it to cool to 40° C. Place a thermometer in each test-tube and determine to within 0.1° C. when the temperatures of the solutions have reached that of the water-bath. Prepare one vessel containing ice and water and another containing hot water. After the contents of the test-tubes have reached the temperature of the water-bath, note the time and with constant stirring, cool the bath at a rate of 2° C. in 5 minutes. Regulate the cooling

by means of cold and hot water. Determine at what temperature the contents of each tube solidifies by frequently inverting them. Plot the concentrations against the solidification temperatures.

Determination of the liquefying temperature—

Allow all the tubes to stand overnight in an ice-chest, and the following day place them in a water-bath at 5° C. When the contents of the tubes attain the temperature of the water-bath, heat it at a rate of 2° C. per 5 minutes. Determine the temperatures at which the gels soften in the manner described, and plot the concentration-temperature curve.

Comparing the solidifying and liquefying temperature-concentration curves, it appears that the liquefying temperatures are far above the solidifying temperatures (Fig. II).

The following table gives an experiment personally conducted by the author :—

Conc. per cent.	Solidification.		Liquefaction.		L — S Graphic In- terpolation.
	Solid.Temp. = S.	Solid. Time Minutes.	Liq. Temp. = L.	Liq. Time Minutes.	
12	21.5	0	27.6	63	6.1
8	19.9	8	26.9	60	7.0
6	17.9	18	26.3	55	8.3
4	14.0(?)	37	24.1	45	9.5
3	12.5	49	21.4	30	10.8
2	6.9	73	19.0	19	11.9
1.5	1.8	98	15.4	0	13.6
1	—	—	—	—	—

The difference between solidification and liquefying temperatures of agar gels is considerably greater than for gelatin gels.

Expt. 110. **Influence of preliminary thermal treatment on gelation**—Divide a 12 per cent. gelatin solution into two portions. Place one portion in an ice-chest and the other in an Erlenmeyer flask. Fit the flask with a cork stopper provided with a capillary tube to prevent vaporization and set in a warm place.¹ After 24 hours bring both solutions to a temperature of 40° C. The gel formed in the ice-chest quickly liquefies and the heated solution cools. Determine, as in Expts. 108 and 109, the time of gelation as well as the solidifying and liquefying temperatures. Considerable difference exists between the properties of these solutions. This phenomenon is readily observed if a 2–3 per cent. gelatin solution is used. These previously treated solutions cooled to room temperature show a distinct difference in the time of gelation. The cooled portion solidifies in 1–2 hours, while the heated solution of the same concentration requires many times that amount for solidification.

Expt. 111. **Influence of acids and alkalis on gelation**—Prepare the following gelatin solutions:

A.	9 c.c. of 3 per cent. gelatin solution	+ 1 c.c. H ₂ O
B.	9 c.c. " " "	+ 1 c.c. $\frac{N}{20}$ HCl
	9 c.c. " " "	+ 1 c.c. 2N HCl
C.	9 c.c. " " "	+ 1 c.c. $\frac{N}{10}$ NaOH
	9 c.c. " " "	+ 1 c.c. 2N NaOH

Place all the solutions in a water-bath at 40° C. for 10–20 minutes and determine the time of gelation or the gelation temperature as in previous experiments.

These additions of acids and alkalis retard gelation measured in the manner described, yet the smaller con-

¹ The same result may be obtained by initially heating to boiling and packing the vessel adequately in cotton, paper, sawdust, etc., in accordance with the principle of the fireless cooker.

centrations also produce an increase in viscosity according to Expt. 71. It is yet to be determined by a more detailed study of gelation whether small concentrations of acids and alkalis exert a gelling influence, or whether an extrapolation of viscosity measurements on the process of gelation is incorrect.

Expt. 112. **Influence of salts upon gelation**—Prepare the following series: 10 c.c. of 6 per cent. gelatin solutions and 10 c.c. of normal solutions of the salts: potassium sulphate, citrate, oxalate, chlorate,¹ chloride, carbonate, nitrate, bromide, cyanide, sulphocyanide, iodide, salicylate, etc., sulphates of potassium, sodium, ammonium, magnesium, calcium,² aluminium, zinc, copper, iron, etc.

Maintain all tubes at 40° C. for 10 to 20 minutes and allow to cool to room temperature. Determine the time required for gelation after the solutions have reached room temperature. These salts give the following series when arranged according to increasing time of solidification:

The potassium salts affect the time of gelation in the order given above; potassium carbonate and the salts preceding it in the series increase the rate of gelation to a greater extent than those following the carbonate when compared with the gelation solution as a control. Cyanides, sulphocyanides, iodides and salicylates of the concentrations given above and at higher concentrations practically retard gelation. These salt-effect series are obtained in weak acid as well as in weak alkaline solutions of gelatin.

The cations with sulphate as anion markedly decrease the rate of gelation. There appears to be no sulphate

¹ Since KClO_3 is not so soluble, the 0.6 g. of gelatin should be dissolved in 20 c.c. of 0.5N KClO_3 solution.

² Saturated $\text{CaSO}_4 = 0.03\text{N}$ at 20° C.

which will retard gelation at this concentration. The cation effect in individual cases varies with the concentration of the salt as well as with the acid or basic reaction of the gelatin solution. The cation effect for weakly acid gelatin solutions gives the series :

Na, Ca, Zn, Mg, Cu, K, NH_4 , Al, Fe ;

and for weakly alkaline gelatin solutions,

Ca, Zn, Cu, Na, Mg, NH_4 , Al, Fe, K.

The salts used were all 0.5N concentration except for CaSO_4 , which was a saturated (0.2 per cent.) solution.

This ionic series, representing their relation effect on gelatin, occurs in colloid chemistry as well as in general physical chemistry and is referred to as the Hofmeister series.

Expt. 113. **Influence of non-electrolytes on gelation**—Determine the time of gelation of the following mixtures (S. J. Levites) :

- | | | |
|---|-----------------------------|--|
| A. 9 c.c. of 6 per cent. gelatin solution | { | + 1 g. urea
+ 1 g. thiourea
+ 1 g. furfural
+ 1 g. chloral hydrate. |
| B. 9 c.c. of 6 per cent. gelatin solution | { | + 1 g. methyl alcohol
+ 1 g. ethyl alcohol
+ 1 g. propyl alcohol
+ 1 g. isobutyl alcohol. |
| C. 9 c.c. of 6 per cent. gelatin solution | + | 1 g. cane sugar. |
| D. 9 c.c. of 6 per cent. gelatin solution | without addition (control). | |

The mixtures in series A lengthen the time of gelation, compared with the control. In series B the higher alcohols likewise retard gelation in proportion to increase in molecular weight. Cane sugar at the concentration given accelerates gelation.

For the theory of gelation, see Expts. 85 and 87.

B. SWELLING

Swelling involves the absorption of a liquid by a solid to form a gel. The process of swelling, like other changes in colloidal state, requires time. The rate of absorption of the liquid is greater at first but gradually decreases. A substance capable of swelling cannot absorb an unlimited

amount of liquid—there is always a swelling maximum. Swelling usually occurs only within a certain temperature range, beyond which the absorbing substance changes into a colloidal solution. Gelatin dissolves in boiling water without first forming a gel. A small portion of a swelling substance goes into solution even at a lower temperature. The property of swelling depends upon certain chemical relations between the absorbing substance and the substance absorbed, e.g. gelatin swells in water and not in chloroform; while rubber

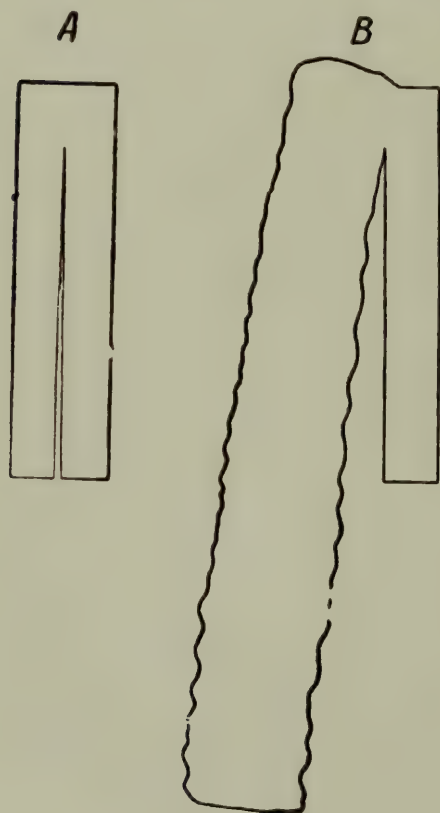


FIG. 12.

behaves in the reverse manner. Addition of other substances exert an influence on the rate and degree of swelling.

Expt. 114. **Qualitative demonstration of the swelling process**—Cut a rectangular strip from thin, cold vulcanized rubber foil used in surgery. Split the rubber

into two large sections (Fig. 12). Dip one portion into a test-tube filled with ether and repeat with chloroform, benzol, etc. The immersed portion shows a considerable enlargement even after a few minutes (Fig. 12, B).

This experiment may be performed with a piece of sheet gelatin, coloured with "Congo red" or "night blue." The gelatin sheet must not be thin, for it easily tears when swollen. The rate of swelling is not as rapid as that of rubber.

The partial swelling of a sheet of glue or gelatin is striking when the lower half is dipped into a dish of water for 24 hours. An experiment, using the thread method, described in Expt. 116, No. 3, is more suitable for the demonstration of the swelling process.

Expt. 115. Qualitative demonstration of swelling in vapour—Lay a very thin, uniformly dried, coloured sheet of gelatin on the table and breathe upon it. The leaf rolls up with a quick motion, so that the surface swollen by the water vapour lies on the outside and the dry unswollen surface on the inside. Allow the sheet to stand until there is no longer any difference in absorption on either side and the leaf will flatten. Fasten a strip of the same gelatin leaf on a support, allowing it to hang freely. Breathe upon one side. A movement in direction of the breath first occurs, the strip remains in this oblique position a short time and then gradually resumes the original position.

Expt. 116. Demonstration of the heat of swelling—Stir about 50 g. of potato meal dried at 105° C. with 50 c.c. of water in a beaker or in a Dewar flask. A thermometer placed in the mixture registers a rise of 10° C. or more in a few minutes.

* * * * *

The simplest method for studying accurately the swelling process involves the determination of the change

in weight, the change in volume, or a dimension of the swelling substance proportionally related to the volume, such as its linear dimension. For determination of the swelling pressure, that is, the force with which the resulting absorption of the fluid can be suppressed, see E. Posniak, *Kolloidchem. Beihefte* **3**, 417 (1912).

1. Weight method (F. Hofmeister); **Preparation of the swelling plates**—To measure the swelling rate by changes in weight, use similar shaped discs of approximately equal weight. For studying the swelling of gelatin, prepare a 40 to 50 per cent. gelatin solution, as in the paragraph preceding Expt. 66. When cool, and still fluid, pour the gelatin over a glass plate, provided with paper strips around the edge. These strips should be glued to the plate with a concentrated gelatin solution and allowed to dry a few days before the experiment is done. Photographic dishes are more convenient, but they must have a smooth plane surface. Make the layer of gelatin solution 0.5–1.0 cm. thick. When using a photographic dish, place it horizontally on a hot plate, to quickly evaporate part of the water. A glass plate with glued paper edges may be used at a moderately high temperature. When the solution has dried sufficiently to give a stiff gel, cut the latter into one or more large pieces and remove it from the dish. Lay the pieces of gel on a clean glass plate. If plenty of material is on hand, round uniform pieces may be punched from the sheet of gelatin with a cork borer. Swelling discs may be obtained more economically by cutting the sheet of gelatin into uniform strips by means of a rule and a sharp knife. The strips are then cut into squares. These discs are usually soft and contain much water. Dry them at a higher temperature, but not high enough to cause softening. The rate of drying is determined by the appearance of contraction figures. Rapid drying forms twig-shaped

depressions on the edges of the disc, which may be decreased in number by reducing the drying temperature. The drying is finished if the discs are clear and show no more loss of weight. The preparation of the plates lasts 2 to 5 days, depending upon their size. Those weighing about 0.5 g. are suitable for most purposes and may be prepared within 1 to 2 days. Use swelling sheets of about the same initial weight for quantitative experiments, since the weight of the discs must be used in calculating the results. After preparation of the discs it is best to weigh the whole material by placing the discs in groups whose difference in weight is 0.05 g. and keeping each group in a separate container. To distinguish between acid and alkaline reactions in the swelling discs a colloid dye such as Congo red may be added to the gelatin solution.

Put the plates in small dishes containing the swelling medium, remove after a definite time, dry carefully with soft filter paper or with a porous plate and weigh. Study the rate of swelling in water vapour by weighing. Use a pulverized swelling substance for this experiment. Place it in a weighing bottle in a desiccator containing a liquid of known vapour pressure. To study the swelling in water vapour, sulphuric acid and water mixtures of various concentrations are suitable. The partial pressure of the water vapour in the sulphuric acid mixtures is given in the table on page 98.

2. **Volume method** (M. H. Fischer)—If the swelling substance is powdered, such as gelatin, agar, fibrin, starch, measure its degree of swelling by increase in volume on swelling in a tube of known or uniform bore. The swelling substance is powdered as fine as possible in a mortar and uniformly mixed. Calibrate the tube and determine the height of the powder in the tube by measur-

Spec. Grav. 15° C.	Per cent. of H SO ₄ .	Relative vapour pressure.
1·746	81·2	0·020
1·659	73·7	0·048
1·559	65·1	0·122
1·479	57·8	0·208
1·426	52·7	0·306
1·374	47·4	0·420
1·329	42·5	0·525
1·289	38·0	0·620
1·242	32·4	0·718
1·202	27·5	0·793
1·162	22·5	0·857
1·113	16·1	0·915
1·052	7·8	0·965
—	—	—
1·000	0·0	1·000

ing with a mm. scale. These results furnish approximate values of the rate of swelling.

An Esbach tube, such as is used for quantitative egg albumin determinations, is suitable. A calibrated test-tube may also be used.

3. **Thread method**—Very simple and reproducible swelling experiments may be performed, if the swelling substance is in the form of a thread.

The enlargement of the thread cross-section may be negligible if the length of the thread be chosen a hundred times greater than the cross-section. This method is more rapid and more economical. The following series of experiments may be used to study the swelling of rubber threads. These threads should not be over 1 mm. thick, preferably thinner and cut as uniformly as possible. Place each thread in a thin-walled glass tube whose inner diameter is about double the thickness of the thread, that is, 2 to 3 mm. These tubes serve as a guide for the

swelling threads. Determine the original length of a thread by laying it on a rule. Place the guide tube with the thread in a small test-tube or combustion tube, 12–15 cm. long and 1.0 cm. diameter. Carefully pour in the swelling medium so that it rises in the guide tube without displacing the thread. Provide the large tube with a tightly-fitting stopper and place the apparatus in a horizontal position (Fig. 13). Measure the resulting elongation of the thread in both directions by means of a rule or scale paper pasted on the tube.

4. **Osmotic method**—The well-known osmometer may be used to measure the swelling of sols. This apparatus consists of a cell with a collodion membrane impermeable to colloids, and one or two tubes suspended perpendicularly therein. A dialysing cup, prepared in Expt. 54, may be used with an earthen or wire net support. Collodion membranes, as well as parchment cups, may be used for these experiments. The volume of these do not remain constant for any length of time. Parchment cups and fish bladders gradually expand, while unsupported collodion cups shrink. Supporting cells about 30 mm. diameter and 90 mm. high prepared from brass or silver wire netting are very practical. The collodion membrane is prepared on the net in the following way: Dip the dry cell into collodion and after drying a short time dip into water to coagulate the collodion layer. Allow the water to drain and pour a collodion layer within and without the cell. Allow to dry for 5 or 10 minutes and coagulate the collodion once again. With porous cells the membrane may be formed directly upon the damp walls as in Expt. 54.

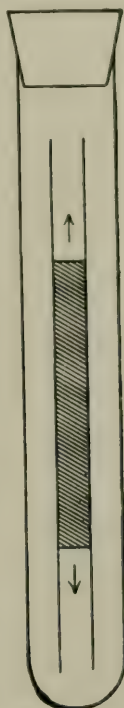


FIG. 13.

The cells are sealed with rubber stoppers, fitted with a perpendicular tube 4 mm. in diameter and which is approximately flush with the lower edge of the stopper (see Fig. 14). To obtain a tighter fit, the bore of the rubber stopper is swollen by moistening with benzene.

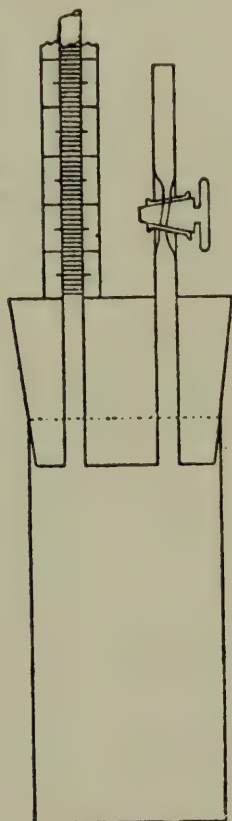


FIG. 14.

The cell should be thickened with collodion at the rim of contact with the rubber stopper. The use of a second short regulating tube fitted with a glass stopcock is more convenient. The cell may be filled while open and the stopper pressed down so as to force the liquid into both tubes, or the cell may be closed when empty and filled through the regulating tube.

A low zero point in the higher tube may be obtained by careful suction through the regulating tube. Place the cell in a large beaker so that it rests on the bottom, in order to decrease the tension on the rubber cork. For accurate results, the beaker should be kept in a thermostat.

* * *

Expt. 117. **Velocity of swelling and swelling maximum**—Perform the following three experiments to gain practice in the methods of obtaining swelling measurements :

(a) Determine the rate of weight increase of two gelatin swelling discs in water by the weight method. The determination of the maximum swelling is difficult by this method, since at this point the sheets are very

brittle and break easily upon drying. However, graphical extrapolation of the maximum swelling value is usually a good approximation.

(b) Place 25 c.c. of water by means of a pipette in a large number of test-tubes about 1.5 cm. in diameter. Arrange the tubes in a support to the height of the water-level in each tube. Use only the tubes which have practically equal diameters. Add 0.2 or 0.5 g. of powdered gelatin, agar, fibrin, etc., to the tubes filled with water by placing the powder on the surface of the water and causing it to sink by tapping the tube. Particles should not adhere to the walls of the tube. The mixture should be shaken at the beginning of each experiment. This method is not suitable for the determination of the rate of swelling, but is adequate for the determination of the swelling maximum. After 24 hours, measure the height of the swollen column by placing a perpendicular scale on the tube. Repeat the measurements, shaking and allowing to settle several times, and take the average.

(c) Allow a thread of rubber to swell in ether, chloroform, xylol, toluol according to the thread method described above. The velocity of swelling as well as the maximum swelling may be determined by using a guide tube of suitable diameter. The maximum swelling is usually attained in 1-2 hours.

(d) Measure by the osmotic method the swelling of 0.5 per cent. gelatin solution placed in HCl and note the lapse of time. A curve is obtained which is related to that in Expts. 117 (a) and 118.

Expt. 118. **Influence of acids and bases on the swelling of gelatin or fibrin**—Determine by the weight method the swelling of gelatin plates in the following solutions:

H₂O; 0.005N HCl; 0.25N HCl.

H₂O; 0.01N NaOH; 0.25N NaOH.

Place the swelling discs in the solutions, note the time and determine the weights. Dry discs weighing more than a gram should be weighed every hour and smaller discs weighed regularly at shorter intervals. At first, a considerable difference is obtained for the rates of swelling of gelatin in acid and alkaline solutions, compared with the rate of swelling in water. Moreover, the swelling maximum does not appear to be directly related to the absolute increase in acid or alkali concentration. The effect of acid and alkali on the viscosity of dilute gelatin solutions (Expt. 71) is such that the viscosity varies directly with the capacity to swell.

The brittleness and deliquescence of the discs in a state of marked swelling give accurate results for the swelling maximum determined by this method. Perform the same experiments with gelatin powder by the volume method. See Wo. Ostwald, *Pflügers Arch. f. Physiologie*, **108**, 563 (1905) for complex absorption-concentration curves.

Study the effect of 0.1N acids and bases on swelling. The absorption maxima decrease, so that the relatively weak dissociated 0.1N acetic acid causes a greater absorption than the strongly dissociated sulphuric acid. It is concluded, therefore, that for decreasing swelling maxima the anion concentration of acids is responsible for this effect rather than the hydrogen ion concentration. Absorption experiments with fibrin by the volume method give the same results (M. H. Fischer).

Expt. 119. **Local acid absorption**—An experiment on the theory of insect stings (M. H. Fischer). Pour a 6 per cent. solution of gelatin into a crystallizing or Petri dish and allow to solidify. Fill a hypodermic needle or a glass tube having a capillary end with formic or acetic acid and stick it into the gel, so that a small amount of acid is left in it. Cover the gelatin with water. The

gelatin is strongly swollen in the places pierced even after 1 to 2 hours (Fig. 15).

Expt. 120. **Influence of salts upon the turgescibility of gelatin**—This may be studied by using neutral gelatin substances just as in the previous experiment. The action of salts on the viscosity of dilute gelatin solutions was studied in Expt. 71. If a 0.125 m. solution is used, the swelling maximum is decreased by sulphates, acetates, tartrates, oxalates, etc., and increased by nitrates, chlor-

ides, bromides, iodides, etc. A series is obtained which Hofmeister in 1890 advanced on the basis of such swelling experiments. By using various salt concentrations, complex curves are obtained. The relation of these curves was studied by Wo. Ostwald,



FIG. 15.

Pflügers Arch., **111**, 581 (1906). Measure the swelling concentration curve for NaCl with gelatin powder by the volume method.

Expt. 121. **Influence of mixtures of acids, alkalis and salts on the swelling of gelatin or fibrin** (M. H. Fischer)—Prepare a series of acid and alkali salt mixtures by starting with 50 c.c. of 0.1N HCl and NaOH and adding to these 50 c.c. of normal salt solution. Observe that in contrast to the salt effect on approximately neutral gelatin, all salts considerably reduce the swelling in both

acid and alkaline media. Moreover, the Hofmeister series applies to acid as well as alkaline solutions in which sulphates, acetates, etc., markedly reduce the swelling, while chlorides, bromides and iodides exert a lesser effect. The volume method is suitable for this experiment.

Expt. 122. **Influence of non-electrolytes on the swelling of gelatin**—Study the effect of 10 per cent. cane sugar and 5 per cent. urea on the swelling of gelatin by the weight or volume method. Sugar retards while urea increases the swelling.

Expt. 123. **Swelling and colloid formation**—Previous studies on the swelling of substances showed that in the range of maximum fluid absorption they become brittle, very soft or viscous. These characteristics of swelling are pronounced in alkaline solutions, in the higher concentrations of the alkali earth chlorides, in solutions of iodides, sulphocyanides, etc., and especially in solutions of urea. These properties are most evident at higher temperatures, hence it is well to conduct the swelling experiments at as low a temperature as possible. Furthermore, the absorption of a fluid by a swelling substance and the solution of that substance by the swelling medium may occur simultaneously during the swelling of the substance.

Determine the amount of gelatin dissolved by the tannin or potassium mercuric iodide method. The tannin test is made by adding 3 drops of freshly prepared tannin solution to 10 c.c. of the acidified swelling solution, which gives a white precipitate. The potassium mercuric iodide test is done by weakly acidifying 5 c.c. of the swelling solution with a drop of sulphuric acid and adding two drops of the concentrated reagent.¹ In a very dilute gelatin solution the milky precipitate becomes visible after the

¹ See Expt. 41 for the preparation of the reagent.

mercuric iodide has settled. According to H. Trunkel¹ the tannin test is positive in concentrations of 1 : 50,000 and the potassium mercuric iodide test, 1 : 125,000.

Increase in swelling capacity is usually followed by an increase in the colloidal solubility. Hence, more gelatin dissolves in acid or alkaline media, in solutions of iodides, urea, etc., than in neutral water or in sulphate solutions. Accurate studies have shown that no direct relations exist between swelling and dissolution, but that both processes are independent of one another (M. H. Fischer). Swelling may be considered as a hydration, dissolution and a dispersion of hydrated colloid particles.

Expt. 124. **Swelling of rubber in various liquids**—Determine by the thread method described above the maximum swelling of rubber threads in the following liquids: water, ethyl alcohol, acetone, amyl alcohol, aniline, ether, benzol, toluol, xylol, and chloroform. Rubber swells slightly or practically not at all in water or ethyl alcohol. The swelling becomes considerable in amyl alcohol and increases with the molecular weight of the alcohol series. The dielectric constants of the rubber solvents decrease in the order given, with the exception of chloroform. Rubber swells in all liquids of small dielectric constants, the values of which are of the order of five or less.

C. SYNÆRESIS

Synæresis is the separation of the disperse phase of a gel from its dispersion medium. This process takes time and yields two separate phases, the solid gel intact, and the clear fluid above it. The best known example of this process is the separation of acidified milk into curds and whey. Uniform gels contract in the course of time with

¹ H. Trunkel, *Biochem. Z.*, **26**, 462 (1910).

the formation of a green-yellow whey. All gels probably show this phenomenon. The separated phase consists not only of the pure dispersion medium, water, but also salts and small amounts of colloid.

Expt. 125. **Synæresis of gelatin, agar, and starch gels**—Prepare the following gels and place them in Erlenmeyer flasks, with well-fitted stoppers:—

6, 3, 1.5, and 1 per cent. gelatin;

3, 1.5, 1, and 0.75 per cent. agar¹;

8, 4, and 2 per cent. starch.

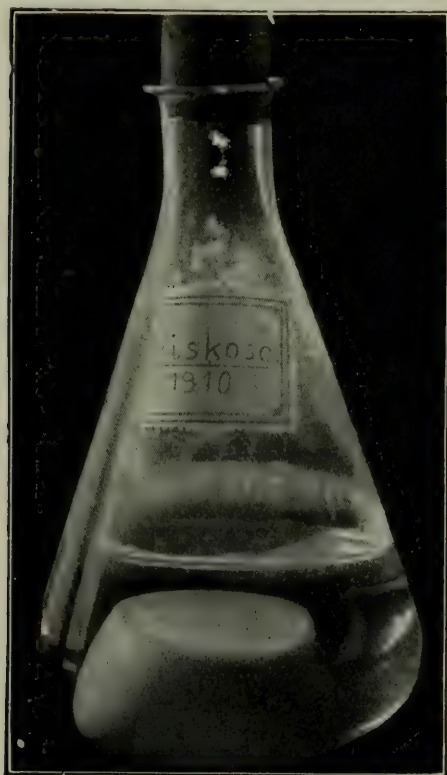


FIG. 16.

The dilute solutions of gelatin and agar gels may be prepared from the concentrated solutions by adding warm water and heating a few minutes to obtain uniform solutions. Prepare the starch paste by sifting the weighed amount through a fine sieve, with a brush, into a small volume of water. Shake continuously, make up to

the required volume and heat 30 minutes on a water-bath.² Add a few grams of thymol to the hot solution to prevent bacterial growth. This gel will keep when cool.

¹ The above concentrations are approximate since it is difficult to obtain agar gels without a residue, which must be separated by filtering through cloth.

² Clump formation cannot be avoided by dipping in boiling water.

A clear fluid separates from the starch, gelatin and agar gels after one or two days. The greatest amount of fluid separates from the more dilute gels, whereas almost no liquid separates from the concentrated gels. Determine the colloid content of the fluid phase from the gelatin gel by the tannin or potassium mercuric iodide method (Expt. 123); from the agar gel with tannin and a few drops of HCl; and from the starch by the iodine reaction.

Expt. 126. **Synæresis of silicic acid gels**—Prepare the following series of gels:

- | | | | | | |
|----|---------|-----------------|----------------|--------|----------------------|
| 1. | 50 c.c. | of 10 per cent. | water glass in | 3 c.c. | 2N HCl ; alkaline. |
| 2. | 50 c.c. | „ | „ | 4 c.c. | 2N HCl. |
| 3. | 50 c.c. | „ | „ | 5 c.c. | 2N HCl ; acid. |
| 4. | 50 c.c. | „ | „ | 6 c.c. | 2N HCl. |
| 5. | 50 c.c. | 3·3 | „ | 3 c.c. | $\frac{2}{3}$ N HCl. |

Add a few drops of phenolphthalein to the water glass before it is mixed with the acid. The amounts of HCl given may be regarded as only approximate, since tests show commercial water glass to contain excess soda. First prepare the approximately neutral mixture (No. 2) and then make up the acid mixtures in the above proportion. All mixtures should solidify at once or within a few hours.

After 24 hours or even a few days, the greatest amount of liquid separated from solutions 1 and 4 and the least from solution 2. Therefore, synæresis is more marked in weak alkaline and acid than in neutral solutions. Observe in the weakly acid colourless solution that the separated fluid has been turned pink by phenolphthalein and hence is weakly alkaline. Comparison between solutions 1 and 5 shows that synæresis of silicic acid is more marked at high concentrations. This is contrary to the synæresis of gelatin, agar, etc.

Test for the SiO_2 content in the decanted fluid with a few drops of copper ammonium hydroxide.

Expt. 127. **Synæresis of a rubber gel during vulcanization** (M. Kröger)—Add 0.6 c.c. of S_2Cl_2 , at room temperature, to 30 c.c. of a 1 per cent. solution of rubber (preferably Hevea crêpe I) in benzine and shake well. The gel formation is complete after 40 minutes, while synæresis begins after 20 minutes. The time varies with the quality of rubber.

D. PRECIPITATION REACTIONS AND RELATED PHENOMENA IN GELS

A chemical reaction which gives a precipitate in a gel rather than in a liquid as a medium may show a great variety of phenomena. Globulites and sphaerolites, etc., sometimes occur instead of crystals with plane surfaces. Large well-formed crystals are produced in other cases. If two solutions are allowed to react by diffusing through a gel under definite conditions, a system of periodically arranged precipitate layers occurs instead of a continuous precipitate. Gas bubbles in gels often have a lenticular shape instead of a spherical one. Many experiments on these phenomena are only qualitative and therefore not easily reproducible. The following experiments have been selected because they can be performed with moderate certainty.

Expt. 128. **Liesegang rings**—Prepare a gel from 4 g. of gelatin, 120 g. of water and 0.12 g. of $K_2Cr_2O_7$; and a solution of 8.5 g. of $AgNO_3$ in 100 c.c. of water. Allow the silver nitrate solution to diffuse into the gel so that the insoluble silver chromate forms in periodic layers. This phenomenon may be illustrated by means of plate, tube or volume experiments.

Plate experiment—Pour a thin layer of bichromate gelatin on a glass, plate or Petri dish and allow it to

solidify. Place a large drop of AgNO_3 in the centre of the gelatin sheet and cover with a dish so that the water will not evaporate too quickly. A series of precipitate rings, as in Fig. 17, form by progressive diffusion. Perform the experiment on an object glass for microscopic study.

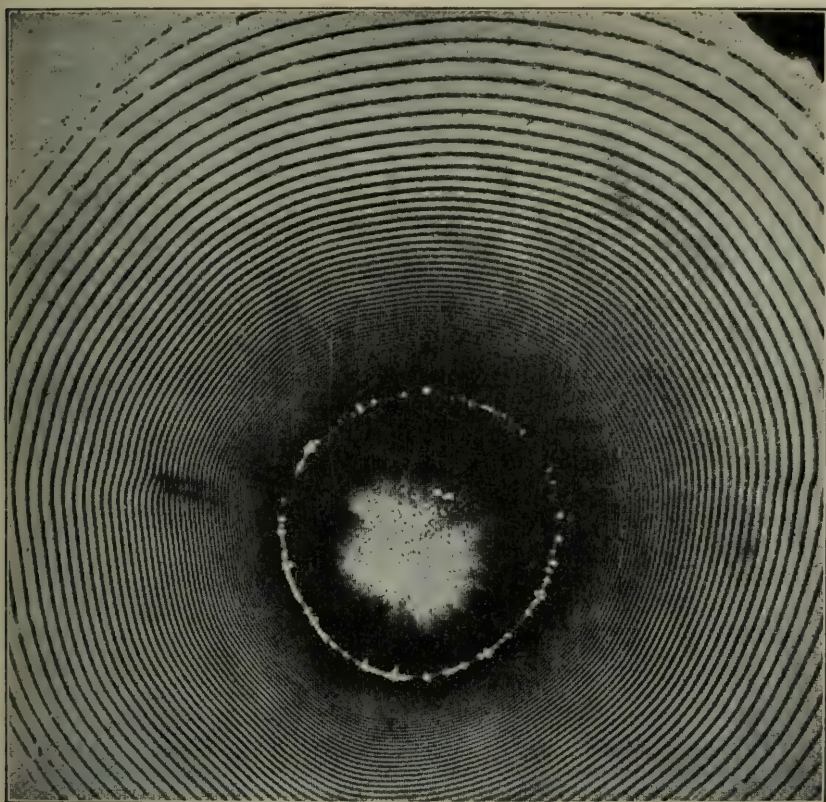


FIG. 17.

Tube experiment—Pour into a test-tube a 15 cm. layer of gelatin and after solidification add a 5 cm. layer of AgNO_3 solution. The $\text{Ag}_2\text{Cr}_2\text{O}_7$, formed by diffusion of the AgNO_3 , separates in thin horizontal layers, the distances between which continuously increase.

Volume experiment—Place some of the bichromate-

gelatin solution in an ice-chest and allow to solidify for 24 hours. Dissolve the gel by dipping it in hot water for a short time or loosen it with a knife. Place the gel in a larger beaker which contains enough silver nitrate to cover it completely. The gel is lighter than the AgNO_3 solution and may be weighted down by laying a glass plate upon it. Allow to stand 1 or 2 days. Larger amounts of gel require a longer time. Then remove the gel from the AgNO_3 solution, wash the outside with cold water and place it in a glass dish. When cut with a sharp knife, the gel gives a cut surface which shows a concentric banding, very similar to that of an agate.

The plate experiment is most suitable when it is to be preserved. The plate may be safely dried in the open, while the tube and volume preparations become dark brown, with consequent loss of the characteristic bands. In the experience of the author, the clearest and greatest number of rings are obtained at room or a lower temperature with the above concentrations.

Expensive silver chromate rings may be replaced by pretty layers of magnesium hydroxide prepared as follows: Swell 3 g. of gelatin, powdered or cut in small pieces, in 300 c.c. of water and dissolve 10 g. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 c.c. of H_2O . Pour 5 c.c. of hot water over the gelatin and after it is dissolved, add the MgCl_2 solution. A 3 per cent. gelatin solution is formed which is normal with respect to MgCl_2 .

Allow to solidify in a test-tube and then add concentrated ammonium hydroxide. A precipitate forms at the interface between the ammonium hydroxide and gelatin, the first isolated ring appearing in a few hours. After one to two days two to three rings appear which are separated from each other by a clear space of more than a centimetre.

Expt. 129. Forms of metallic lead precipitates in

Expt. 132. **Cluster-shaped precipitate membranes**—Fill a tall narrow beaker with a saturated solution of potassium ferrocyanide and carefully place a few drops of CuSO_4 solution upon the surface by means of a dropping tube. The drop, which must remain upon the surface of the cyanide solution, becomes surrounded with a perfectly transparent membrane of copper ferrocyanide.

This membrane thickens so much in the course of an hour, that the copper sulphate drops appear enveloped in a

2. Initially transparent but which finally becomes solution brown and opaque.

3. Perform the same experiment with a 3-6 per cent. acetic solution of gelatin, which has been heated several hours (dense boiling water-bath so that it may gel spontaneously.) Phenol this solution by drops into a 5 per cent. aqueous colomin solution. Colourless white sacs form, which become dark and non-elastic after a few hours.

4. These precipitate membranes are protected with a thin layer of gel and are the prototypes of those "semi"—

4. "selective"—permeable membranes, which play so important a rôle in the theory of osmotic pressure and in general Physiology.

Expt. 133. **Gas bubbles in gels**—Add a few drops ammonium carbonate solution to 20 c.c. of a 10 per cent. water-glass solution, and pour the mixture into equal volume of acetic acid. A particularly clear solution which solidifies in a few hours and which produces gas bubbles during solidification.

Larger gas bubbles may be produced by heating the silicic acid gel a short time before its solidification. Gas bubbles may be formed in a 10-15 per cent. gelatin gel if carbonate is first added and acetic acid allowed to diffuse in after solidification. [E. Hatschek.]¹

¹ In the experience of the author the experiment may be carried out with 3-6 per cent. gels to which are added, before gelling, a

gelatin solution in an ice-chest and allow to solidify for 24 hours. Dissolve the gel by dipping it in hot water for a short time or loosen it with a knife. Place the gel in a larger beaker which contains enough silver nitrate to cover it completely. The gel is lighter than the AgNO_3 solution and may be weighted down by laying a glass plate upon it. Allow to stand 1 or 2 days. Larger amounts of gel require a longer time. Then remove the gel from the AgNO_3 solution, wash the outside with cold water and place it in a glass dish. When cut with a sharp knife, the gel gives a cut surface which shows a concentric banding, very similar to that of an agate.

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Perform the same experiment with a 3-6 per cent. solution of gelatin, which has been heated several hours on a boiling water-bath so that it may gel spontaneously. Add this solution by drops into a 5 per cent. aqueous tannin solution. Colourless white sacs form, which become dark and non-elastic after a few hours.

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The bubbles at the time of formation or somewhat later may be spherical, but usually are double convex lens-shaped, which later become disk-shaped.

The causes of these divergent shapes is probably due to the specific "cleavage" of the gels and to the unequal pressure produced by the forming bubbles. If these preparations are preserved for a long time, the lens-shaped gas bubbles gradually assume a spherical shape. The first formed lens-shaped gas bubbles are partially filled with synæretic liquid. Enlargement of these lens-shaped spaces is a consequence of synæresis, the gas bubbles moving back and forth in the cleft space when the test-tube is inclined.

E. DRYING AND FREEZING OF GELS

Expt. 134. **Figure formation in the drying of egg white** (O. Bütschli, M. H. Fischer)—Pour a few c.c. of fresh egg white into a small glass dish with a smooth plane bottom to form a layer 0.5–1 c.c. deep. Allow the egg white to dry in the open air or in a desiccator. Polygonal plates appear in the former and very fine spiral cracks may be observed in the latter preparation. Microscopic analysis with a Nicol prism shows colour phenomena similar to those observed with starch grains.

Expt. 135. **The drying of gelatin solutions**—Smear a few large cover-glasses with a 6 per cent. solution of warm gelatin and allow them to dry in a warm place, such as an asbestos plate warmed by a small burner. Observe that the cover-glasses are bent by the contracting gel. The glass breaks with increased drying. Pour a small amount of the same solution upon a strong glass plate and put the plate in a drying oven at 100° C. After few drops of $2\text{N}(\text{NH}_4)_2\text{CO}_3$ and covered over with dilute acetic acid.

the gelatin is dry, dissolve it with concentrated or with a few drops of saturated potassium cyanide or sodium

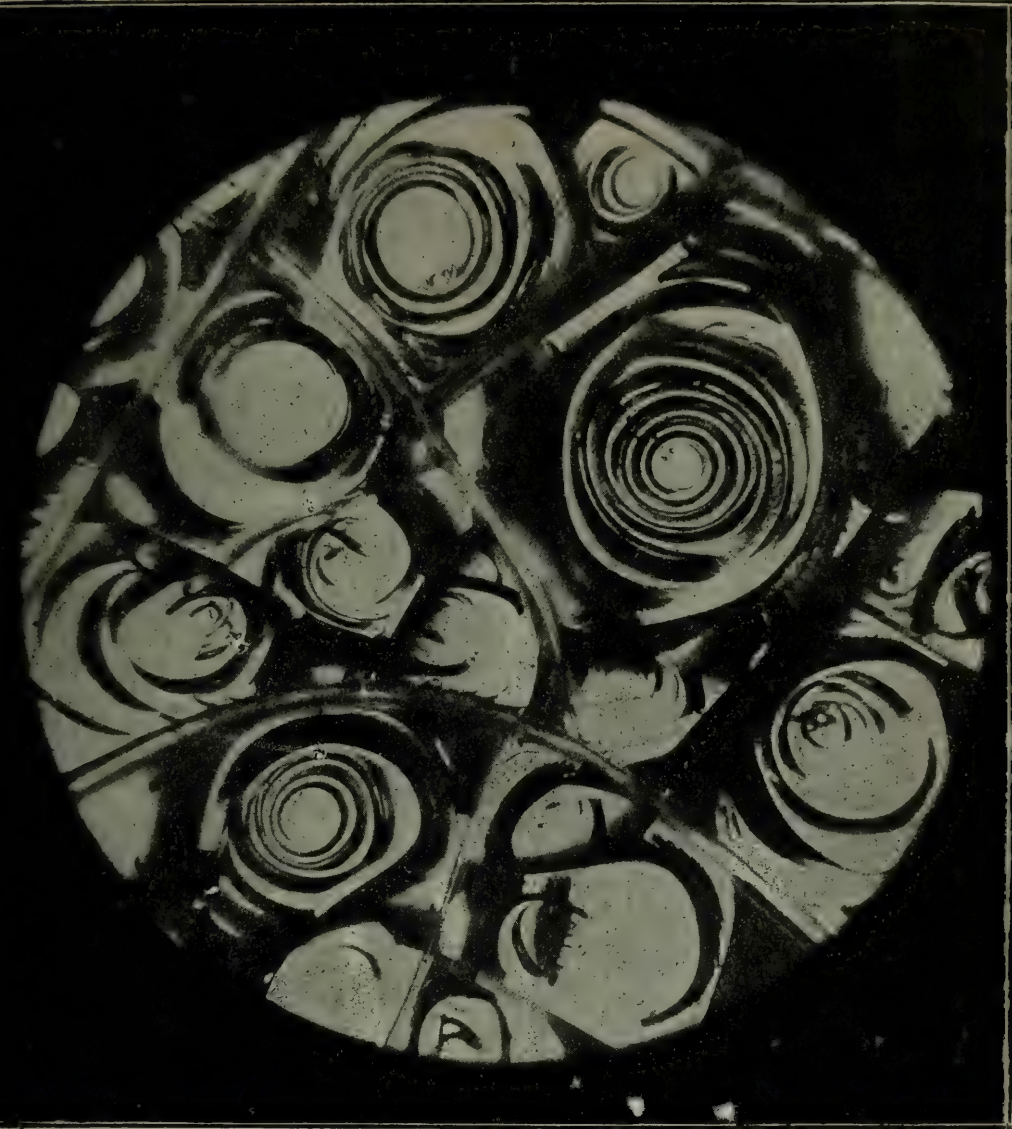


FIG. 18.

salicylate and wash the plate clean with a brush. Observe that the drying gelatin etched large shell-shaped figures in the glass.

Solutions of animal glue are usually better than gelatin. The gelatin or glue must have complete contact with the glass in order to obtain good results. Better contact is assured by roughening the glass plate with hydrofluoric acid.

Expt. 136. **Ice crystals in gelatin gels**—Pour a few c.c. of hot 6–10 per cent. gelatin solution on a well-cleaned glass plate. Drain the excess gelatin so that a very thin layer remains on the plate. After the gel solidifies, put the plate where the temperature of the air is a few degrees below freezing. The formation of large ice crystals requires a long period at freezing temperature. The water, crystallizing to form the well-known ice flowers, compresses the gelatin in such a way that a gelatin “pseudomorphosis” results with “negatives” of the ice crystals. Allow the plate to come to room temperature to evaporate the water. The shapes stamped in the gelatin remain intact.

H. Ambronn uses gum arabic instead of gelatin in this experiment.

VII

ADSORPTION

ADSORPTION involves the change in the concentration of the disperse phase at the interface. Increase in concentration or positive adsorption is most frequent. Molecular disperse solutions, colloids and coarsely disperse systems can adsorb, that is, form more concentrated solutions at their interfaces. Adsorption may take place at different kinds of interfaces. In a system consisting of a disperse phase in a liquid dispersion medium, adsorption by the disperse phase may take place by contact with solid bodies such as charcoal, by contact with fluids such as shaking with chloroform, and by contact with gases afforded by the available surface of dispersoids. Adsorption is greatest when the interfaces in a system are greatest. Therefore, the specific external surface, that is, its extent divided by the volume or weight of the adsorbent, must be as large as possible. Solid adsorbents are often chosen in the form of powder, fluids as drops and gases as bubbles. When shaking a solution with the adsorbent the concentration changes in the solution should be uniform and rapid throughout the system.¹

¹ After the condensation of a molecular disperse substance upon an interface, diffusion into the adsorbent follows. The latter phenomenon was referred to as "Absorption." According to Davis, iodine is adsorbed by charcoal, but on further contact is absorbed. W. McBain introduced the term "Sorption" to

A. ADSORPTION AT THE INTERFACES OF
A LIQUID AND SOLID

Expt. 137. **Qualitative demonstration of adsorption**—Pour into a series of Erlenmeyer flasks, 50 c.c. of faintly coloured solutions of FeCl_3 , $\text{Cu}(\text{NH}_4)_2(\text{OH})_2$, $\text{K}_2\text{Cr}_2\text{O}_7$, fuchsine, crystal violet, brilliant green, methyl violet, etc., that is, molecular disperse systems, and also faintly coloured solutions of $\text{Fe}(\text{OH})_3$, silver, gold, graphite, Prussian blue, Congo red, night blue, that is, colloidal systems. Add a gram of blood or bone charcoal to each of these flasks. Shake several times and filter the mixtures through ordinary folded filters. If the solutions have not been too concentrated, a practically colourless filtrate is obtained in each case.

For demonstration purposes the mixtures may be poured in a large filter, so as to obtain large amounts of colourless filtrate. Fill a glass tube 3 cm. wide and 20 cm. long with bone charcoal and provide with an outlet. Filter the coloured solutions one after another through a column of charcoal.

Expt. 138. **Proof of the presence of adsorbed dyes at the interfaces**—The disappearance of the colouring material upon shaking with charcoal cannot be accepted as final proof that the interface is responsible for the process. The decolorization may consist of a chemical decomposition of the disperse phase by the charcoal. It may be proven qualitatively in the following way that

designate the whole series of phenomena in order to include thereby all their associated characteristics. All absorption phenomena are preceded by adsorption and the latter is more universal. Therefore, a consideration of the complex nature of this class of reactions has led the author from the term "sorption" to that of "adsorption" in accord with the general practice.

such is not always the case in adsorption as in Expt. 137. Shake 50 c.c. of a 0.01N solution of "brilliant green" with enough charcoal (0.5–1.0 g.) to completely decolorize the solution and filter. Pour a portion of the charcoal from the residue into a test-tube containing water, another portion into a test-tube containing alcohol and shake each. The water remains colourless after the charcoal settles, while a green colour is imparted to the alcohol after shaking with the charcoal. This experiment shows, therefore, that the decolorizing of the brilliant green solution was not due to a chemical decomposition of the disperse phase, but that the dye had actually permeated the interface of the charcoal and liquid and could be removed again by a suitable solvent (Expt. 142).

Expt. 139. **Surface colours of adsorbed dyes** (H. Freundlich)—The occurrence of surface colours is an indication of the extraordinarily high concentration which dyes can attain by adsorption on charcoal. Charcoal saturated with dyes in a damp state usually has a bronze shade. Shake 100 c.c. of a 1 per cent. solution of crystal violet with a gram of charcoal and filter. The damp charcoal in the filter shows a brown or greenish-bronze shimmer similar to that of the dry pure dye. Shake some charcoal with water, filter, and compare the colour of the residue with the previous one containing adsorbed dye.

Expt. 140. **Adsorption of lead nitrate by animal charcoal**—Shake 50 c.c. of a 0.07 per cent. solution of lead nitrate with a gram of animal charcoal and filter. The lead nitrate solution before adsorption gives a heavy precipitate with potassium chromate. After adsorption by the charcoal, the filtrate gives no precipitate with potassium chromate, and a slight yellow colour with H_2S . The lead nitrate was almost completely adsorbed under the above experimental conditions.

Expt. 141. **Adsorption of alkaloids by aluminium**

silicate—Naturally occurring aluminium silicates, such as kaolin, ordinary earth, distinct from alumina (Al_2O_3), the so-called Fuller's earth or white kaolin, show a pronounced ability to adsorb alkaloids. The alkaloid, quinine sulphate, is adsorbed to the greatest extent.

Quantitative data on the amounts of adsorbent and adsorbed material are difficult to obtain, since the adsorbing capacity of the aluminium silicate varies with the commercial modes of preparation. Fuller's earth and ordinary clay prove to be effective adsorbents of alkaloids in the experiences of the author. Shake 50 c.c. of 0.1 per cent. quinine bisulphate solution with 10 g. of pulverized air-dried clay, filter and prove that adsorption has occurred by testing the filtrate with potassium mercuric iodide.

Expt. 142. **Influence of dilution. Reversibility of adsorption**—Place 50 c.c. of about 0.05N acetic acid in each of four Erlenmeyer flasks. Add 50 c.c. of water to flasks 1 and 2, add three grams of charcoal to 2, 3 and 4 and shake about five minutes. To flask 3 add 50 c.c. of water and shake again for 5 minutes. Filter the contents of 2, 3 and 4, remove with a pipette 50 c.c. from flask 1 and from the filtrates of 2 and 3 and 25 c.c. from filtrate 4. Titrate the solutions with 0.1N NaOH and phenolphthalein. The experiment may be illustrated from table on opposite page.

The figures below were obtained from one of such experiments.

The results of flasks 2 and 4 show that the amount of acetic acid adsorbed by 3 g. of charcoal depends only on the concentration of the material to be adsorbed. The same amount of acetic acid was present in both flasks, but in 2 it was dissolved in twice as much water as in 4. That is, the same amount of adsorbed material was present only in half the concentration. Observe that the con-

Number.	1	2	3	4
0.05N acetic acid c.c.	50	50	50	50
Water added c.c.	50	50	0	0
Charcoal added g.	0	3	3	3
Additional amounts of water . c.c.	0	0	50	0
Filtered	—	+	+	+
Amounts titrated c.c.	50	50	50	25
Results in 0.1N NaOH. . . . c.c.	12.24	5.41	5.45	4.14
Acetic acid adsorbed	0	6.83	6.79	8.10

centration of the adsorbed substance is proportional to the amount adsorbed, since less of the same absolute amount of acetic acid was adsorbed from the dilute solution 2 than from the concentrated solution 4. The absolute adsorbed amounts of acetic acid are in the proportion of 8.1 : 6.83. The comparison between 2 and 3 appears even more striking. The weight of acetic acid first adsorbed from 3 was equal to that adsorbed from 4, but so much water was added that the final concentration became equal to that of solution 2. Therefore a part of the adsorbed acetic acid returns into solution upon additional dilution, reversibility of this type of adsorption, so that the absolute amount of adsorption is the same (6.83 : 6.79) with equal end concentrations. The amount of adsorption is determined by the final concentration of the solution regardless of other concentration proportions previously existing in the mixture.

Expt. 143. **Quantitative adsorption of acetic acid**
 —Pour into six Erlenmeyer flasks the following amounts of dilute acetic acid. Prepare, approximately, the concentrations given by diluting 2N acid :—

Number.	1	2	3	4	5	6
C.c. of solution . . .	150	150	150	125	110	105
Normality	0.012	0.025	0.05	0.1	0.2	0.4

Determine by titrating with 0.1N NaOH and phenolphthalein the accurate content of acetic acid in each solution. For these titrations, remove with a pipette 5 c.c. of solution from 6, 10 c.c. from 5, 25 c.c. from 4 and 50 c.c. from 1, 2 and 3, so that 100 c.c. of solution remain in all the flasks.

Add to each flask, exactly 3 or 5 g. of animal charcoal and shake the whole series for 5 to 10 minutes. Filter the contents of each flask separately and determine the amount of acetic acid in the filtrate by pipetting and titrating the amounts given above. The following personally conducted experiment describes how the results were arranged.

In Fig. 19 the results are recorded graphically. The

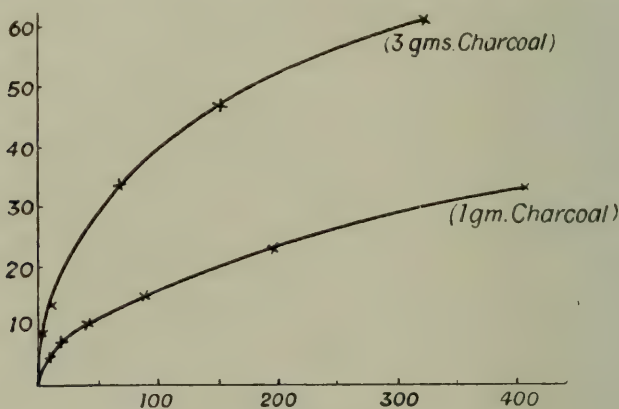


FIG. 19.

equivalent concentrations are plotted as abscissæ ($c-x$) and the amounts adsorbed (x) as ordinates, on a scale five times as large. The adsorption curve shows that

relatively more of the disperse phase is adsorbed from a dilute solution than from a concentrated one and that at higher concentrations the amounts adsorbed approach a maximum called the "adsorption maximum."

The characteristic first portion of the curve corresponds approximately with the adsorption formula $x = k(c-x)^n$, where x represents the acetic acid adsorbed by a given amount of charcoal, c the original concentration and $c-x$ the equivalent or final concentration after adsorption, K and n two constants. For testing this formula

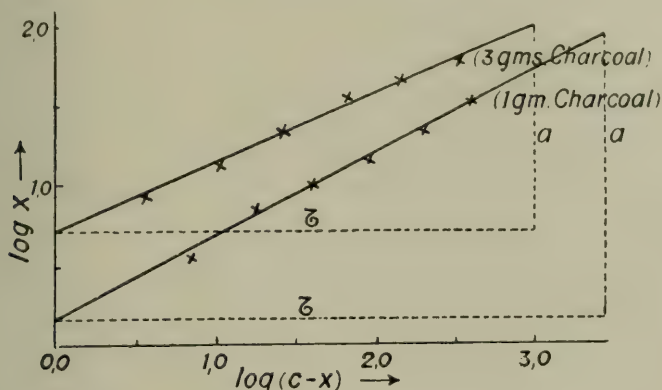


FIG. 20.

and for calculating the results use the logarithmic form of the equation, $\log x = \log K + n \log (c-x)$. This is the equation of a straight line which cuts the $\log x$ -axis at a distance $\log K$ and makes an angle with the $\log (c-x)$ axis whose tangent is equal to n . Record on a coordinate system the values of $\log (c-x)$ as abscissæ and values of $\log x$ as ordinates, as shown in Fig. 20. If the equation proves to be correct the points must lie approximately on a straight line (Fig. 20). Draw a straight line through as many adjacent points as possible. The values of the constants K and n must first be determined in order to use the equation numerically. $\log K$ is equal to the space which the straight line cuts off on the $\log x$ -axis

(Fig. 20). The values for the example submitted are 0.17 and 0.72; the corresponding numbers for K are, therefore, $K_1 = 1.48$, $K_3 = 5.18$. The tangents of the angles are equal to the quotient of the distances $a : b$ (see figure). These distances are taken for maximum accuracy and give the values $n_1 = 0.49$ and $n_3 = 0.43$ in the results plotted. Substitute the two numerical constants in the above logarithmic formula and calculate x .

If Fig. 20 is plotted on a very large scale ¹ the calculated value for $\log x$ may be read directly from the plotted figure. Erect perpendiculars from a chosen point on the $\log (c-x)$ axis. The ordinate value of the point where the perpendicular cuts the straight line is equal to $\log x$ calculated.

These simple exponential formulæ or Boedecker "adsorption formulæ" give correct quantitative values for only relatively dilute solutions. Experimentally and theoretically, the observed concentration differences $(c-x)$ in equal weights of moderately and highly concentrated solutions do not indicate the amount actually adsorbed. The following equation holds good for such cases:—

$$\frac{N}{m} (c_0 - c) = K c^n (100 - c),$$

where N is the weight of the solution in grams, m the grams adsorbed, c_0 the original concentration and C the equivalent concentration after adsorption has taken place, both calculated in per cent. (Wo. Ostwald and R. de Izaguirre). This equation gives a maximum concentration difference or "apparent" amount adsorbed in moderately concentrated solutions and the "apparent" adsorption equals zero in a 100 per cent. solution. This

¹ The graph may be constructed advantageously on large sheets of co-ordinate paper pasted on cardboard and the results plotted with a soft pencil so that they may easily be erased.

Charcoal = 1 g. ; Solution = 100 c.c.

c Original concentration in c.c. of 0.1N NaOH per 100 c.c. of solution.	$c-x$ Equilibrium concentration after adsorption in c.c. of 0.1N NaOH per 100 c.c. of filtrate.	x Amount adsorbed in c.c. of 0.1N NaOH per 100 c.c. of solution.	$\log (c-x)$	$\log x.$	x	
					Experimental.	Calculated.
12.0	7.3	4.7	0.863	0.672	4.7	4.5
26.0	18.9	7.1	1.277	0.851	7.1	7.1
52.3	42.3	10.0	1.626	1.000	10.0	10.5
105.2	90.5	14.7	1.957	1.167	14.7	15.3
220.8	198.2	22.6	2.297	1.354	22.6	22.4
444.8	411.7	33.1	2.615	1.520	33.1	32.1

$K = 1.48. \quad n = 0.49.$

Charcoal = 3 g. ; Solution = 100 c.c.

12.2	3.6	8.6	0.556	0.934	8.6	9.0
24.4	10.8	13.6	1.033	1.134	13.6	14.4
49.4	27.8	22.4	1.431	1.350	22.4	21.4
100.4	66.8	33.6	1.825	1.526	33.6	31.6
198.5	151.5	47.0	2.180	1.672	47.0	45.0
385.8	326.6	59.2	2.514	1.772	59.2	62.6

$K = 5.18. \quad n = 0.43.$

equation represents cases which seldom occur in practice and assumes that only the disperse phase and not the dispersion medium is adsorbed. Nevertheless, such is the general case. A discussion of this equation is given by Wo. Ostwald and R. de Izaguirre in *Koll. Zeitschr.*, **30**, 279 (1922).

Expt. 144. Adsorption of Crystal ponceau and methylene blue by wool ; L. Pelet-Jolivet (electro-

chemical adsorption)—Use a 0.2 per cent. aqueous solution of crystal ponceau and a 0.05 per cent. solution of methylene blue to prepare the following mixtures :

Crystal ponceau : 1. 10 c.c. of solution.

2. 10 c.c. ,, ,, + 10 drops 2N HCl.

3. 10 c.c. ,, ,, + 10 drops 2N NaOH.

Methylene blue : 4. 10 c.c. of solution.

5. 10 c.c. ,, ,, + 10 drops 2N HCl.

6. 10 c.c. ,, ,, + 10 ,, 2N NaOH.

Place a few white wool fibres in these mixtures, leave them 20 to 30 minutes at room temperature and then wash thoroughly with cold water. Observe that the wool fibres are not affected by the basic or neutral solutions but are distinctly coloured by the acidified dye, crystal ponceau. The reverse occurs in the methylene blue solution. There is an indistinct colour adsorbed from the fibre by the acid dye, a distinct colour with the neutral dye and a very intense colour with the alkaline solution.

These results may be explained by electrical or electrochemical considerations. The wool is charged negatively in the presence of an excess of (OH^-) ions and positively in excess of (H^+) ions. This is the case with other relatively indifferent substances (J. Perrin). Crystal ponceau is an acid and methylene blue a basic dye. If the wool carries a definite positive charge in acid medium, the oppositely charged anion of the acid dye, crystal ponceau, is adsorbed. Conversely, in an alkaline medium, the wool is negatively charged and the positively charged cation of the basic dye, methylene blue, is adsorbed. Wool is a weak acid and exists in water in the form of a massive negatively charged anion in association with the hydrogen ion. In a neutral medium, the wool should show an alkaline reaction toward both dyes ; the experi-

ment shows this to be the case.¹ In contrast with the adsorption of acetic acid by charcoal, this electro-chemical adsorption is irreversible (L. Michaelis).

Use filter paper strips instead of wool. Choose a shorter time of reaction or a more dilute solution, else the difference in the reaction is insignificant.

Expt. 145. **Specific dye adsorption by silicic acid and aluminium hydroxide gels**—The pure commercial preparation “asmosil” or Patrick’s “silica gel” may be used as the SiO_2 gel, while the commercial native alumina is a suitable $\text{Al}(\text{OH})_3$ gel. These gels may be prepared by pouring water glass into concentrated HCl and aluminium chloride into ammonium hydroxide. Thoroughly wash the two gels. Fill two test-tubes or flasks with a few grams of SiO_2 gel, two others with $\text{Al}(\text{OH})_3$ gel. Test the properties of the gels with a 0.01 per cent. solution of methylene blue and a corresponding solution of “patent blue.” Allow the mixtures to stand a while and decant or wash into a filter. The silicic acid gel has irreversibly adsorbed the “methylene blue” and has not at all or only faintly adsorbed the “patent blue.” Conversely, the aluminium hydroxide gel has strongly adsorbed the “patent blue,” but has only faintly adsorbed the methylene blue.

B. ADSORPTION AT THE INTERFACE OF TWO LIQUIDS

Expt. 146. **Adsorption of colloidal copper sulphide at the interface, water-chloroform** (W. Biltz)—Prepare two copper sulphide hydrosols as follows:

A. Add 1–2 c.c. of a dilute solution of copper sulphate

¹ Further data is given by L. Pelet-Jolivet and co-workers in *Koll. Z.*, **2**, 225 (1905), which contains a complete bibliography, or in *The Theory of Dyeing*, by the same author, Dresden, 1910.

or copper chloride to a mixture of 90 c.c. H_2O + 10 c.c. of freshly saturated hydrogen sulphide water, until a weakly turbid dark-brown sulphide sol is attained.

B. To a similar mixture of water and hydrogen sulphide, add drop by drop, 1-2 c.c. of a dilute solution of copper ammonium hydroxide. Prepare the latter by mixing the $CuSO_4$ solution used in A with NH_4OH until the resulting precipitate again dissolves to give a clear solution. A dark-brown sol is obtained, but it is clear in contrast to the sol prepared in A.

Shake 15 c.c. of both sols with 2-3 c.c. of chloroform. Sol A is completely decolorized after shaking for a few seconds. The copper sulphide is adsorbed at the interface, water-chloroform, and sinks with the chloroform. Sol B is only slightly decolorized after much longer shaking.

The reaction of the sols is the cause of this difference in behaviour. Sol A is acid and sol B is alkaline as a result of their modes of preparation. If sol B is weakly acidified so that it is not flocculated within 1 to 2 hours, it may be adsorbed like sol A.

To obtain the sol in the upper layer of the mixture, the experiment should be performed with benzol.

Expt. 147. **Adsorption of gelatin at the interface, water-benzol**—Prepare a dilute gelatin solution which gives a distinct precipitate with the tannin test—10 c.c. of solution + 1 c.c. of 10 per cent. tannin solution + 1 c.c. dilute H_2SO_4 . A 0.001 per cent. gelatin solution is suitable. Shake 15 c.c. of this solution with 5 c.c. of benzol or xylol for at least 5 minutes and filter the white emulsion through a moistened filter paper.¹ Perform a tannin test on the clear filtrate in exactly the same way as before, shaking the solution with benzol. The tannin reaction, if it has not disappeared, has become consider-

¹ If the filter paper is not previously wetted the pores are clogged by the benzol, with consequent slowing of the filtration.

ably weaker than before adsorption. Therefore adsorption of the gelatin has taken place at the surface of the benzol drops.

Expt. 148. **Adsorption of a coarsely disperse powder, such as charcoal at the interface, liquid-liquid**—Prepare a 1 per cent. aqueous suspension of animal charcoal, by previously grinding it as uniformly as possible. The suspension settles slowly. Shake about 15 c.c. of the suspension with benzene, xylol, chloroform, carbon tetrachloride, etc. An almost quantitative adsorption of charcoal particles occurs at the interface between water and the liquids named.

Expt. 149. **Separation of coarsely disperse mixtures by selective adsorption at the interface, liquid-liquid (Flotation)**—Prepare a finely-ground mixture of 9 parts of animal charcoal and 1 part of aluminium silicate such as clay. Shake 2-3 g. of this mixture with 100 c.c. of water to form a suspension and decant once or twice from the coarse particles of clay which may be present. The suspension should appear black or greyish black. Shake this suspension with one of the liquids mentioned in the previous experiment, such as benzol. The charcoal, not the clay, is adsorbed at the interface, benzol-water. The mixture separates into two sharply-defined layers when poured into a test-tube. The upper benzol layer is coloured black by the charcoal adhering all around it and not by internal absorption. The lower aqueous layer is coloured greyish white by the clay which remains unadsorbed. A sharp separation of the mixture is thus produced.

This experiment demonstrates the typical phenomenon of a series of technical processes known as "flotation" and have attained great importance and development in recent years. This process consists in freeing and purifying graphite from the earthy gangue by shaking with a

suitable hydrocarbon. Sulphide ores are also concentrated at such liquid-liquid interfaces, but other substances are concentrated at the liquid-gas interfaces, while gangue-like substances remain behind in the aqueous dispersion medium. The application of this process is due to its ability to accomplish extensive disintegration of material. Sludges are too difficult to handle by the usual smelting process and may be recovered by this method.

The following simple experiment demonstrates the essentials of many flotation processes:

Expt. 150. **Flotation of printed and unprinted pieces of paper**—Cut a few pieces from a printed, sized paper; a few from a sheet unprinted on either side, and a few from a heavily-printed page. Shake these pieces in water contained in an Erlenmeyer flask until they sink to the bottom. Cover the water with a thin layer of light mineral oil, the dispersion medium of black print, and shake vigorously. After separation of the layers, observe that the printed pieces remain in the upper layer, with the black printed side upward, while the unprinted pieces of paper remain at the bottom of the flask.

C. ADSORPTION AT THE LIQUID-GAS INTERFACE

Expt. 151. **Peptone membranes**—Weigh 1 g. of peptone and dissolve it in 200 c.c. of distilled water to give a 0.05 per cent. solution. Put about half the solution in a crystallizing dish about 15 cm. in diameter. Dilute a portion of the remainder ten times (0.005 per cent.) and fill a crystallizing dish of similar size with this solution. Float a new, thin sewing needle upon the surface of the liquid in each dish by holding the needle in the middle with dry finger-tips, immersing them gently into the liquid and carefully releasing the needle. Bring a

horseshoe magnet near the needle without touching it. Withdraw the magnet rapidly so as give the needle a rotatory motion. The needle oscillates through an arc of a few degrees and then comes to rest. The needle itself is not magnetic and automatically assumes a polar orientation.

Allow the needle to float undisturbed upon the peptone solution for 20 to 30 minutes and repeat the magnet experiment. Observe that the needle still rotates when under the influence of the magnet. If this magnetic influence is not too strong, the needle will not come to rest in a new position, but will again return to the original position. This backward rotation is not due to polar attraction but to the peptone accumulating in a higher concentration at the interface of the peptone solution and water vapour. This interface assumed the properties of an elastic membrane, that is, a thin gel membrane which is not discernible by the naked eye.

This membrane forms more rapidly in more concentrated solutions. However, it may be formed in a very dilute solution after about 24 hours. At the end of this period, the membrane of a 0.05 per cent. solution is so strong that the needle will only move when the magnet is very close to it. Its motion is usually longitudinal, not lateral or rotatory. Tear the membrane around the needle with a glass rod. The needle now behaves toward the magnet as in the beginning of the experiment.

Another modification of the experiment is to use a sewing needle magnetized by stroking. Such a needle maintains polar orientation on the surface of a fresh solution during rotation of the dish. After the solution stands 20-30 minutes, the polar adjustment becomes slower and rather indefinite. After 24 hours, the membrane is usually so rigid that the dish may be turned in any desired position without the needle being able to resume polar orientation.

VIII

COAGULATION, PEPTIZATION AND RELATED PHENOMENA

COAGULATION is the decrease in the degree of dispersion of colloidal solutions by formation of microscopic and larger particles. This process results in a settling of the coarsely disperse particles with a simultaneous decrease in the volume of the dispersion medium. The particles in a stable colloidal solution remain dispersed because of a definite hydration or solvation with the dispersion medium. The process of coagulation involves a decrease in this hydration and hence a mutual separation of the two phases. Un-flocculated colloids are termed sols, while coarsely disperse colloids are known as gels. There are a number of methods for the flocculation of a colloidal system. The phenomena studied in the previous experiments involved flocculation by the addition of electrolytes.

The size of the particles which determine the state of coagulation cannot be defined because of the great number of transitions possible between colloid and coarsely disperse particles. Flocculation, like all colloid changes of state, require time, but the rate of flocculation may vary considerably, depending upon the experimental conditions. Therefore, flocculation can never be defined like gelation in terms of such values as flocculation point, concentration, time or temperature. However, the course of flocculation may be followed by plotting curves of the

rate of change in the size and degree of solvation of the coalescing particles. A direct accurate method consists of ultramicroscopic counting of the number of particles in a given volume of sol during flocculation. This method is applicable only to sols completely resolvable ultramicroscopically and is only practical in certain cases. There are other direct methods of more general application. Another simple principle, of use in these flocculation experiments, is to follow the rate of sedimentation. If the right and left arms of a U-tube are filled with equal volumes of two liquids having different densities, the heights of the liquid columns vary inversely as their densities. If the density of one of the liquids changes, then the difference in level will change until the densities of both liquids become equal. Such a density change occurs in a coalescing solution if the upper liquid decreases in the concentration of the disperse phase. The two-armed flocculation apparatus involves this principle (Fig. 21).¹ It consists of a U-tube 130 cm. long, as shown

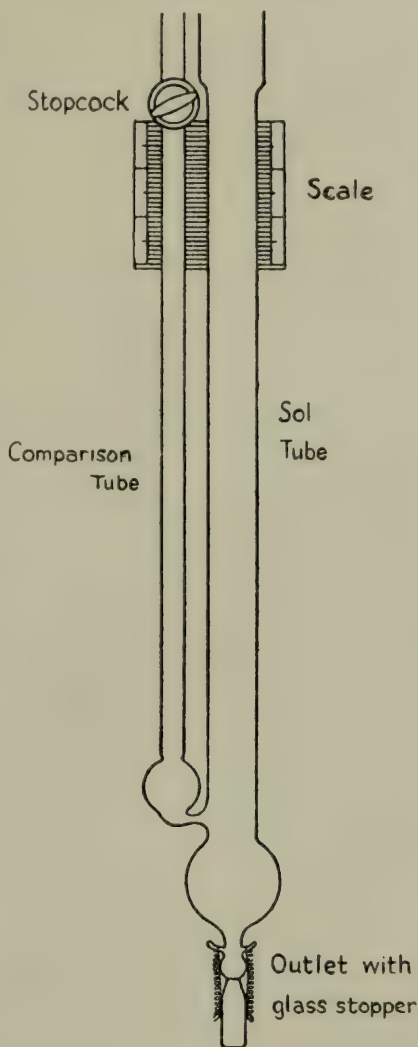


FIG. 21.

the two-armed flocculation apparatus involves this principle (Fig. 21).¹ It consists of a U-tube 130 cm. long, as shown

¹ Wo. Ostwald and F. V. v. Hahn, "On a Kinetic Flocculation Meter," *Koll. Z.*, **30**, 62 (1922).

in the figure. The narrow arm, 3.7 mm. wide, is called a comparison tube and is provided with a stopcock above and a bulb blown at the lower end. Beyond the bulb there is a constriction leading to the wider tube of 6 mm. diameter. The constriction prevents mixing of the comparison liquid with the sol to be studied. The sol tube has a bulb just below the opening of the comparison tube. The lower end of the sol tube consists of a pear-shaped appendage, 8 cm. long and 8–10 mm. wide, terminating in an outlet closed with a ground-glass stopper. The upper end of the sol tube is somewhat widened to obviate bubble formation on filling. The readings are made by means of a scale, 130 cm. high extending a mm. below the bulb of the comparison tube.

The procedure is as follows: First, add the comparing liquid, such as distilled water, to the apparatus until it reaches the 120 cm. mark in both arms. Close the stopcock in the smaller arm and open the glass stopper at the bottom of the large tube. The sol tube is emptied and the comparing liquid remains in the smaller tube because of the constriction. Rinse the tube with the sol and fill it up to the 115 cm. mark. Then open the stopcock and observe the displacement of the two liquids. Read the difference in height at definite time intervals, depending upon the rate of flocculation and the accuracy desired. These differences may be calculated from the readings on the comparison tube. The single arm flocculation tube is more sensitive, especially against temperature variations.

The following coagulation measurements on a mercury sulphide sol in the double arm flocculation tube are illustrative.

There are a number of simpler indirect methods for determining the rate of flocculation. These methods depend upon gradual changes of a physico-chemical

Time after addition of coagulant Minutes.	Height in sol tube. mm.	Height in com- parison tube. mm.	Difference.
2	1272.4	1312.2	39.8
4	1272.4	1312.2	39.8
6	1272.4	1312.2	39.8
7	1272.4	1312.2	39.8
8	1272.4	1312.2	39.8
9	1273.2	1310.4	37.2
10	1273.6	1309.6	36.0
12	1274.1	1308.7	34.6
15	1275.1	1306.9	31.8
18	1275.7	1305.8	30.1
22	1276.8	1303.8	27.0
26	1277.4	1302.6	25.2
30	1277.9	1302.5	24.6

property of the sol during flocculation, i.e. turbidity, surface tension, viscosity, etc. Examples of such changes during coagulation are given below.

The kinetic methods involving a continuous change in one of the properties during coagulation have as yet not been sufficiently developed. As a result, the determination of coagulation points is more prevalent. Indirect results may be obtained as follows: Determine (1) the concentration of an added substance which will produce a marked change in the turbidity of a sol in a given time, i.e. within 1, 2 or 24 hours; (2) the concentration of an added substance at which a microscopic flocculation is produced; (3) the concentration at which the disperse phase is held back by filter paper with pores of uniform size; (4) the concentration at which the flocculating system attains either a colour shade or turbidity of a prepared comparison solution, etc.

A. FLOCCULATION OF SUSPENSIDS

Electrolyte coagulation of typical suspensoids is characterized by the small absolute concentration of electrolyte necessary for precipitation. This frequently amounts to only a few millimols of electrolyte per litre of sol. The valence of the coagulating electrolyte is of great importance. In general, a colloid is precipitated by a much smaller concentration of polyvalent than monovalent ions. Furthermore, the sign of the charge on the colloid is also significant. In the case of positively charged colloids, the valence and the nature of the negatively charged anions influence flocculation. Conversely, the cations have a similar influence on negatively charged colloids. The absolute concentrations of the electrolytes precipitating a colloid depend upon the conditions of preparation of the sol, the degree of dispersion, the concentration, etc. Since concentration varies with temperature, determinations made on the same sols under defined conditions would be comparable.

Expt. 152. **Qualitative demonstration of the electrolytic flocculation of suspensoids**—Fill two similar large cylindrical or preferably parallel walled vessels either with mastic sol prepared in Expt. 1 or with dilute black India ink. Pour a few c.c. of concentrated alum solution into one of the vessels, stir and allow to stand undisturbed. Large white curds appear in the vessel containing the electrolyte within 20–30 minutes. More rapid flocculation may be produced either by using a clear As_2S_3 sol, prepared in Expt. 12, or a semi-transparent solution of commercial collargol. A large addition of alum causes a distinct turbidity immediately or within a few minutes. Examine the sol microscopically and observe that the identity of the sol is gradually obscured

by addition of electrolyte, whereas upon lateral inspection, the sol radiates light more intensely.

Flocculation may be demonstrated qualitatively by using the sensitive red gold sol, which changes colour at once upon addition of a few c.c. of HCl or alum. A 0.01 per cent. solution of Congo rubin may also be used to demonstrate the sudden change upon addition of almost any electrolyte with a subsequent coarser flocculation within a few hours.

Expt. 153. **Electrolytic flocculation of negative arsenic trisulphide sols**—Prepare about 50 c.c. of a clear As_2S_3 sol, as in Expt. 12. Pipette 10 c.c. of the sol into a series of well-cleaned test-tubes having practically the same diameter. Into another series of test-tubes place by means of a 10 c.c. graduated hand burette various electrolyte solutions, such as HCl, KCl, CaCl_2 , AlCl_3 , K_2SO_4 , potassium citrate, diluted with water so that the total volume of each solution will be just 10 c.c. Pour each salt solution into a tube containing the As_2S_3 sol and thoroughly mix by pouring the solutions back and forth a few times. Thus, 20 c.c. of the reaction mixture half sol and half electrolyte is obtained. The following series of mixtures serve as an example.

As_2S_3 obtained by passing H_2S into 500 c.c. of a 0.5 per cent. As_2O_3 solution for 5 minutes.

(a) HCl.

2.5 c.c. 0.1N HCl	+ 7.5 c.c. H_2O	+ 10 c.c. As_2S_3 sol	= 12.5 millimols	
5.0 c.c. „ „	+ 5.0 „ „	„ „	= 25 „	
1.0 c.c. 1N „ „	+ 9.0 „ „	„ „	= 50 „	
2.0 c.c. „ „	+ 8.0 „ „	„ „	= 100 „	

(b) KCl.

5.0 c.c. 0.1M KCl	+ 5.0 c.c. H_2O	+ 10 c.c. As_2S_3 sol	= 25 millimols	
0.5 c.c. 2.0M KCl	+ 9.5 „ „	„ „	= 50 „	
1.0 c.c. „ „	+ 9.0 „ „	„ „	= 100 „	
2.0 c.c. „ „	+ 8.0 „ „	„ „	= 200 „	

(c) CaCl_2 .

0.5 c.c.	0.01M CaCl_2	+9.5 c.c.	H_2O	+10 c.c.	As_2S_3 sol	=0.25 milli-	mols
1.0 c.c.	"	+9.0	"	"	"	= 0.50	"
2.0 c.c.	"	+8.0	"	"	"	= 1.00	"
4.0 c.c.	"	+6.0	"	"	"	=2.00	"

(d) AlCl_3 .

0.5 c.c.	0.001M AlCl_3	+9.5 c.c.	H_2O	+10 c.c.	As_2S_3 sol	=0.025 milli-	mols
1.0 c.c.	"	+9.0	"	"	"	= 0.050	"
2.0 c.c.	"	+8.0	"	"	"	= 0.10	"
4.0 c.c.	"	+6.0	"	"	"	=0.20	"

(e) $\frac{1}{2} \text{K}_2\text{SO}_4$.

0.5 c.c.	1.0N K_2SO_4	+9.5 c.c.	H_2O	+10 c.c.	As_2S_3 sol	= 25 milli-	mols
1.0 c.c.	"	+9.0	"	"	"	= 50	"
2.0 c.c.	"	+8.0	"	"	"	= 100	"
4.0 c.c.	"	+6.0	"	"	"	=200	"

(f) $\frac{1}{3} \text{K}_3$ citrate.

0.6 c.c.	2.0N K_3 citrate	+9.4 c.c.	H_2O	+10 c.c.	As_2S_3 sol	=62.5 milli-	mols
1.25 c.c.	"	+8.75	"	"	"	= 125	"
2.5 c.c.	"	+7.5	"	"	"	= 250	"
5.0 c.c.	"	+5.0	"	"	"	=500	"

The concentration of the electrolyte which causes a distinct turbidity immediately or after one hour may be regarded as the flocculation value. Thus, in the previous experiment, the sol did not immediately become turbid with KCl at 25 millimolar concentration, but distinctly so with a concentration of 50 millimols. The flocculation value lies between the two concentrations and may be accurately determined by the use of intermediate concentrations.

The figures in heavy type show that in the above example, the flocculation values of the three chlorides are approximately as 80 : 0.8 : 0.08 or as 1000 : 10 : 1. The trivalent Al^{+++} ion is by far the strongest electrolyte, since the least concentration is required to flocculate the

sol. K_2SO_4 and potassium citrate behave like KCl and their flocculation values are approximately of the same magnitude. HCl is not really a strong flocculant and remains far below the flocculation values for $CaCl_2$ and $AlCl_3$. These results indicate that the cation or positively charged ions are responsible for the flocculation values for a negative arsenic trisulphide sol and that the activity of the cations greatly increases with their valence. The following tables show the flocculation values of other electrolytes. It indicates also that the valence of the cation does not play the only rôle. Determine, for example, the flocculation value of the univalent morphine chloride (mol. wt. 321.5).

Other sulphide sols, negatively charged metal sols and mastic sols, behave like the As_2S_3 sols.

 FLOCCULATION OF As_2S_3 SOLS.

Electrolyte.	According to H. Schulze.	According to S. E. Linder and H. Picton.	According to H. Freundlich.
Univalent cations, $c =$ millimols per litre.			
(Acetic acid)	ca. 14900)	—	—
($\frac{1}{3}$ H_3PO_4)	ca. 1290)	—	—
($\frac{1}{2}$ oxalic acid)	ca. 373)	—	—
($\frac{1}{2}$ H_2SO_3)	ca. 275)	—	—
$\frac{1}{3}$ K_3 citrate	—	—	> 240
K acetate	—	—	110
$\frac{1}{2}$ Li_2SO_4	—	124.4	—
$LiNO_3$	—	109.0	—
$LiCl$	185.4	—	58.4
$\frac{1}{4}$ $K_4Fe(CN)_6$	181.2	—	—
Sodium acetate	154.3	—	—
$\frac{1}{2}$ K_2SO_4	151.0	123.1	65.6
$\frac{1}{2}$ pot. oxalate	131.2	—	—
KNO_3	117.6	104.7	50.0
$\frac{1}{2}$ Na_2SO_4	109.0	137.4	—
KI	107.3	102.2	—
NaI	—	117.0	—
$\frac{1}{3}$ K_3 tartrate	104.3	—	—

FLOCCULATION OF As_2S_3 SOLS (*continued*).

Electrolyte.	According to H. Schulze.	According to S. E. Linder and H. Picton.	According to H. Freundlich.
$\frac{1}{3} K_3Fe(CN)_6$	100.5	—	—
$NaNO_3$	100.4	110.8	—
KCl	97.9	[97.9]	49.5
$KClO_3$	92.7	—	—
NH_4NO_3	90.5	73.9	—
NH_4I	—	73.9	—
NH_4Br	—	73.9	—
NH_4Cl	90.3	62.9	42.3
KBr	81.5	101.0	—
$NaBr$	—	109.0	—
$NaCl$	80.6	103.5	51.0
$\frac{1}{2} (NH_4)_2SO_4$	80.4	95.8	—
$\frac{1}{2} H_2SO_4$	80.0	92.4	30.1
HNO_3	57.5	57.5	—
HCl	49.4	58.7	30.8
HI	—	57.5	—
HBr	—	56.0	—
Guanidine nitrate	—	—	16.4
$\frac{1}{2} Ti_2SO_4$	8.36	1.60	—
Strychnine nitrate	—	—	8.0
Aniline chloride.	—	—	2.52
p.-Chloraniline chlor- ide	—	—	1.08
Morphine chloride	—	—	0.425
New fuchsine	—	—	0.114

Bivalent cations, c = millimols per litre.

$MgSO_4$	3.16	2.10	0.810
$[Fe(NH_4)_2(SO_4)_2]$	3.03	—	—
$MnSO_4$	2.31	2.02	—
$FeSO_4$	2.77	2.02	—
$CoSO_4$	—	1.96	—
$ZnSO_4$	1.86	1.68	—
$NiSO_4$	1.88	1.65	—
$CaSO_4$	2.64	1.60	—
$NiCl_2$	—	1.52	—
$CdCl_2$	—	1.46	—
$FeCl_2$	—	1.42	—
$Co(NO_3)_2$	—	1.37	—

FLOCCULATION OF As_2S_3 SOLS (*continued*).

Electrolyte.	According to H. Schulze.	According to S. E. Linder and H. Picton.	According to H. Freundlich.
ZnCl ₂	—	1·34	0·685
CaCl ₂	2·06	1·31	0·649
Ca(HCO ₃) ₂	1·95	—	—
CaBr ₂	—	1·31	—
MgBr ₂	—	1·31	—
CoCl ₂	—	1·29	—
Sr(NO ₃) ₂	—	1·29	—
Ca(NO ₃) ₂	—	1·29	—
SrCl ₂	—	1·23	0·635
Cu(NO ₃) ₂	—	1·23	—
BaCl ₂	1·68	1·18	0·691
MgCl ₂	1·05	1·14	0·717
Ba(NO ₃) ₂	1·84	1·14	0·687
CdCl ₂	—	1·01	—
UO ₂ (NO ₃) ₂	—	—	0·642
CdBr ₂	—	0·954	—
CdSO ₄	—	0·924	—
CuSO ₄	—	0·911	—
Cd(NO ₃) ₂	—	0·899	—
HgCl ₂	—	0·322	—
PbCl ₂	—	0·225	—

Trivalent cations.

$\frac{1}{2}$ Fe ₂ (SO ₄) ₃	—	0·216	—
$\frac{1}{2}$ Cr ₂ (SO ₄) ₃	—	0·154	—
CrCl ₃	0·316	—	—
FeCl ₃	0·123	0·136	—
$\frac{1}{2}$ Nd(SO ₄) ₃ ,	—	0·080	—
$\frac{1}{2}$ Pr ₂ (SO ₄) ₃	—	—	—
$\frac{1}{2}$ Al ₂ (SO ₄) ₃	0·112	0·074	—
$\frac{1}{2}$ La ₂ (SO ₄) ₃	—	0·074	—
$\frac{1}{2}$ Ce ₂ (SO ₄) ₃	—	0·074	0·092
AlCl ₃	0·090	0·062	0·093
Al(NO ₃) ₃	—	—	0·095
NH ₄ Fe(SO ₄) ₂	—	0·102	—
KCr(SO ₄) ₂	0·141	0·092	—
KAl(SO ₄) ₂	0·077	0·040	—
KFe(SO ₄) ₂	0·063	—	—
NH ₄ Al(SO ₄) ₂	—	0·040	—

Expt. 154. **Electrolytic flocculation of copper sulphide hydrosol**—Prepare a copper sulphide sol (Expt. 146) by dropping dilute copper ammonium hydroxide into dilute H_2S water and pour 20 c.c. of the mixture into an Erlenmeyer flask. A drop of this sol is placed upon a filter paper by means of a glass rod. If a thin uniform light brown spot forms, the sol is negative (Expt. 105). If the sol does not spread uniformly but forms a "mirror" or a small spot with sharp edges surrounded by a larger circle, it is too coarsely disperse and the experiment does not apply. Add from a burette containing normal KCl or $MgCl_2$, successive, small definite amounts of electrolyte, shake, and after each addition, test on filter paper. A concentration is soon attained at which the sol no more spreads uniformly over the paper, but forms a "mirror" with sharp edges and is surrounded by a ring of the colourless dispersion medium. This concentration of electrolyte added may be accepted as the precipitation value.

If a series of mixtures are prepared simultaneously as in Expt. 153, the precipitation value may be determined by the formation of a sharply defined zone on suspended strips of paper.

Expt. 155. **Electrolytic flocculation of a gold sol**—Metals in the colloidal state often show a sudden colour change as a first indication of flocculation. Red colloidal gold turns blue-violet to blue; yellow or brown colloidal silver changes to red, violet and blue respectively (Expt. 94). A coarsely disperse flocculation appears in a short time as a sequence to the colour changes.

Determine as in Expt. 153 the concentration of HCl , $MgCl_2$, and $AlCl_3$ necessary to transform a red gold sol into a blue-violet within ten minutes.

Expt. 156. **Electrolytic flocculation of Congo rubin**—Flocculations accompanied by sudden colour

changes are followed more conveniently with Congo rubin than with gold sols, when studying the gold number. According to Expt. 97, Congo rubin in a 0.01 per cent. solution suddenly changes to blue-violet with almost all electrolytes of certain concentrations. Flocculate the Congo-rubin dye solution with baryta or saturated sodium hydroxide solution. The colour change and flocculation produced by these alkalis is not a chemical change due to the liberation of a different coloured acid dye, since acids also yield similar results. High hydroxyl ion concentrations do not produce this chemical change. Nevertheless, the colour change and precipitation of the dye take place.

For quantitative determination of the flocculation values as with the As_2S_3 sol, Expt. 153, pipette equal volumes, e.g. 1 c.c. of the dye solution into a series of clean test-tubes. Prepare salt mixtures similar to those in Expt. 153 and make them up to a volume of 9 c.c. Mix the dye with the salt solutions by repeatedly pouring the contents of the tubes back and forth. The salt concentration which produces flocculation shows a distinct colour change toward red-violet or violet-blue after an hour. The indication of flocculation by colour transition becomes well defined with a little practice. A solution for colour comparison may be prepared either by mixing methyl violet or azoblue with acid fuchsine or by using a Congo-rubin sol at the colour transitions of flocculation.

These absolute precipitation values vary with the preparation of the dye. Nevertheless, they all show a relative difference in flocculating values similar to inorganic sols illustrated in the table below:¹—

¹ For further data, see *Kolloidchem. Beihefte* 12, 94 (1920).

Electrolyte.	Flocculation value in millimols per litre.	Molar precipitation in litre of sol flocculated by a litre of electrolyte. ¹
KCl	95.9	10.4
MgCl ₂	1.67	597.7
AlCl ₃	0.245	4082.
$\frac{1}{2}$ Na ₂ SO ₄	61.2	16.4
MgSO ₄	0.394	2538.
$\frac{1}{2}$ Al ₂ (SO ₄) ₃	0.03	33333.

The effect of the cations on flocculation values is as evident here as with the As₂S₃ sols; while polyvalent cations have greater flocculating power, the anion must not be neglected. Sulphates flocculate more strongly than chlorides.

Expt. 157. **Flocculation of ferric hydroxide sol**—Use a positively charged ferric hydroxide sol, prepared in Expt. 22, or a commercially prepared sol freed from excess of chloride ion by warm dialysis. Applying the same methods as in the previous experiments, especially Expt. 153, determine the flocculation values of NaOH, KCl, CaCl₂, AlCl₃, K₂SO₄, K₃-citrate. The following data are representative of an experiment performed by the author:

Fe(OH)₃ sol, dialysed. Fe₂O₃ content = 0.506 per cent.

(a) NaOH.

1.0 c.c. 0.01N NaOH + 9.0 c.c. H ₂ O + 10 c.c. Fe(OH) ₃ sol = 0.5 millimols			
2.0 c.c. ,, + 8.0 c.c. ,, ,, ,, ,,			= 1.0 ,,
4.0 c.c. ,, + 6.0 c.c. ,, ,, ,, ,,			= 2.0 ,,
8.0 c.c. ,, + 2.0 c.c. ,, ,, ,, ,,			= 4.0 ,,

¹ The term "Molar precipitation in litre of sol flocculated by a litre of electrolyte" refers to the number of litres of colloid which can be flocculated by a mol of the electrolyte.

(b) KCl.

0.5 c.c.	2N KCl	+ 9.5 c.c.	H ₂ O	+ 10 c.c.	Fe(OH) ₃ sol	=	50 millimols
1.0 c.c.	"	+ 9.0 c.c.	"	"	"	=	100 "
2.0 c.c.	"	+ 8.0 c.c.	"	"	"	=	200 "
4.0 c.c.	"	+ 6.0 c.c.	"	"	"	=	400 "

(c) $\frac{1}{2}$ CaCl₂.

0.5 c.c.	2N CaCl ₂	+ 9.5 c.c.	H ₂ O	+ 10 c.c.	Fe(OH) ₃ sol	=	50 milli- mols
1.0 c.c.	"	+ 9.0 c.c.	"	"	"	=	100 "
2.0 c.c.	"	+ 8.0 c.c.	"	"	"	=	200 "
4.0 c.c.	"	+ 6.0 c.c.	"	"	"	=	400 "

(d) $\frac{1}{3}$ AlCl₃.

2.0 c.c.	3N AlCl ₃	+ 8.0 c.c.	H ₂ O	+ 10 c.c.	Fe(OH) ₃ sol	=	300 milli- mols
4.0 c.c.	"	+ 6.0 c.c.	"	"	"	=	600 "
8.0 c.c.	"	+ 2.0 c.c.	"	"	"	=	1200 "

(e) K₂SO₄.

1.0 c.c.	0.01M K ₂ SO ₄	+ 9.0 c.c.	H ₂ O	+ 10 c.c.	Fe(OH) ₃ sol	=	0.5 milli- mols
2.0 c.c.	"	+ 8.0 c.c.	"	"	"	=	1.0 "
4.0 c.c.	"	+ 6.0 c.c.	"	"	"	=	2.0 "
8.0 c.c.	"	+ 2.0 c.c.	"	"	"	=	4.0 "

(f) K₃ citrate.

1.0 c.c.	0.005M K ₃ citrate	+ 9.0 c.c.	H ₂ O	+ 10 c.c.	Fe(OH) ₃ sol	=	0.25 millimols
2.0 c.c.	"	+ 8.0 c.c.	"	"	"	=	0.5 millimols
4.0 c.c.	"	+ 6.0 c.c.	"	"	"	=	1.0 millimols

Compare these flocculation values with those for As₂S₃ (Expt. 153). KCl in both cases flocculated at concentrations of the same order of magnitude. On the other hand, the flocculation value of bivalent CaCl₂ and especially of trivalent AlCl₃ are considerably lower with As₂S₃ sol; the flocculation value of CaCl₂ is almost the same as that of KCl for Fe(OH)₃ sol, and that of AlCl₃ is greater. The flocculation values of K₂SO₄ and potassium

citrate are of the same order of magnitude as that of KCl for As_2S_3 , but a considerably smaller concentration is necessary for the $\text{Fe}(\text{OH})_3$ sol. The HCl has a strong flocculating activity for the As_2S_3 , while NaOH is particularly active for the $\text{Fe}(\text{OH})_3$ sol. Thus, for the $\text{Fe}(\text{OH})_3$ sol, the anion determines the flocculation values, while the cation determines the flocculation values for the As_2S_3 . The behaviour of Congo rubin resembles more that of the As_2S_3 sol, yet the simultaneous action of both ions of the flocculation electrolyte may be distinctly recognized.

The aluminium hydroxide sol behaves like the ferric hydroxide sol.

Expt. 158. **“ Abnormal series ” with mastic sol**—This term refers to the phenomenon whereby the same electrolyte may have a flocculating or non-flocculating effect upon a given sol, depending upon its concentration. It may be logical to suppose that a dilute flocculating electrolyte would have a still greater effect if it were added in a larger concentration. However, particularly with multivalent electrolytes, this assumption does not hold. There is a flocculation range of concentrations referred to as the first flocculation zone; then follows a range of concentrations in which no flocculation occurs referred to as the non-flocculation zone, and finally the recurrence of a second flocculation zone.

Prepare a mastic sol by pouring 10 c.c. of a 5 per cent. alcohol solution of mastic into 90 c.c. of water. Dilute this concentrated sol ten times (0.05 per cent.) and filter. Pipette 5 c.c. of the sol into each of a large number of well-cleaned test-tubes. Pour 10 c.c. of a molar solution of aluminium chloride into a ten c.c. graduated cylinder. Add half of this solution to the first test-tube containing the mastic sol and shake the mixture. Fill the graduated cylinder with water, halving the concen-

tration of the aluminium chloride and add 5 c.c. to the second tube of mastic sol, etc., as illustrated in the table below :—

FLOCCULATION OF 0.05 PER CENT. MASTIC HYDROSOL BY AlCl_3 OF VARIOUS CONCENTRATIONS.

No.	AlCl_3 concentration in millimols per litre of mixture.	Flocculation after 24 hours.	No.	AlCl_3 concentration in millimols per litre of mixture.	Flocculation after 24 hours.
1	500	Completely flocculated	12	0.25	Not flocculated
2	250	" "	13	0.125	" "
3	125	" "	14	0.064	Flocculated
4	64	" "	15	0.032	Completely flocculated
5	32	" "	16	0.016	" "
6	16	" "	17	0.008	Somewhat turbid
7	8	Slightly flocculated	18	0.004	Not flocculated
8	4	Somewhat turbid	19	0.002	" "
9	2	Not flocculated	20	0.001	" "
10	1	" "	21	0.0005	" "
11	0.5	" "	22	0.00025	" "

Beginning with the smallest concentration of AlCl_3 solution, and gradually increasing it, the first flocculation appears between 0.008 and 0.064 millimolar concentration. Then a non-flocculation zone extends to a concentration of 4 millimols. Flocculation again appears with an increase in the concentration of the AlCl_3 unto the second concentration zone.¹

An insight into the theory of this striking phenomenon is obtained by an electrophoretic experiment, utilizing the ultramicroscopic method first with the sol alone, without addition of salt, and then with the sol + AlCl_3 at a concentration within the non-flocculation zone. The sol possesses a negative charge, while the sol containing AlCl_3 has a positive charge in the non-flocculating zone.² The electric charge on the mastic hydrosol may

¹ It is understood that on repeating the experiment there will be changes in the absolute concentration values.

² The positive sol in the non-fluctuating zone appears to give

be neutralized by the addition of AlCl_3 of definite intermediate concentrations. With smaller AlCl_3 concentrations, a mastic sol behaves like a negative As_2S_3 sol, while with higher AlCl_3 concentrations, it behaves like a positive ferric hydroxide sol.

Expt. 159. **Influence of temperature on the flocculation of Congo rubin** (compare with Expt. 97) —Add 5–10 c.c. of a normal KCl solution to 50 c.c. of a 0.01 per cent. solution of Congo rubin and pour some of the mixture into three test-tubes. Place one tube in ice water, allow the second to remain at room temperature and place the third in a water-bath at about 50°C . Flocculation by the electrolyte occurs first at 0°C ., much later at room temperature, and does not take place at 50°C .

REVERSIBILITY OF FLOCCULATION OF SUSPENSIDS

Most electrolytes precipitate suspensoids irreversibly. It is impossible to wash out the electrolyte and again change the gel into a sol. In some cases the irreversibility of flocculation is not so much a property of the colloids as that of the flocculating electrolyte. Thus, colloidal silver, according to S. Odén and E. Ohlon [*Zeitschr. für physik. Chem.*, **82**, 78 (1913)], may be reversibly flocculated by ammonium nitrate. Colloidal sulphur, which is classed between typical suspensoids and emulsoids, is reversibly flocculated by most alkali salts. The reversibility of such flocculations may be demonstrated conveniently by Congo rubin, described in Expt. 97.

up its charge easily. On passage of current no cation migration is noticeable in the first 20–30 seconds, but after 1–2 minutes the direction of migration becomes evident.

The phenomenon of peptization, i.e. washing the gel as described in Expts. 30–34, is an example of the reversibility of electrolyte-flocculated suspensoids.

Expt. 160. **Flocculation of suspensoids by dialysis**—In the preparation of colloid solutions described in the chapter preceding Expt. 30, the presence of a small amount of electrolyte is necessary for the stability of most suspensoids. If the maximum concentration of these “sol-forming” ions is exceeded, the colloid flocculates. Hence, caution must be taken in many cases not to carry the dialysis too far. Suitable examples of flocculation by dialysis are: first, mercury sulphide hydrosols prepared from $\text{Hg}(\text{CN})_2$ (Expt. 14); second, copper sulphide hydrosols prepared from copper ammonium hydroxide (Expt. 146); third, cadmium sulphide hydrosols (Expt. 3); fourth, positive sols, particularly ferric hydroxide sols (Graham). Dialyse 40–50 c.c. of the $\text{Fe}(\text{OH})_3$ sol in an analytic dialyser (Expt. 54). Compare with the undialysed sol kept at the same temperature. The $\text{Fe}(\text{OH})_3$ sol flocculates in the dialyser after 24 hours. Concentrated $\text{Fe}(\text{OH})_3$ sols form jelly-like precipitates.

Expt. 161. **Flocculation by an electric current**—An electrophoresis experiment continued for a long time causes the colloid to flocculate on the electrode to which it is attracted. This phenomenon may be clearly observed by ultramicroscopic electrophoresis. Study the electrophoresis of silver and mastic sols and allow the electrical contact to last only a few minutes. Coarsely disperse, strongly reflecting flocculates may be observed, accompanied by the appearance of dark patches, i.e. colloid-free spaces in the field of vision.

For flocculation by adsorption, see Expt. 146.

B. FLOCCULATION OF EMULSOIDS

The flocculation of hydrated emulsoids is characterized by the very high concentrations of neutral salts required. The reason for this difference in salt concentration is that the flocculating electrolyte not only coalesces the particles into greater aggregates, but also causes a dehydration of the colloid particles, i.e. a partial separation of the dispersion medium adsorbed by these particles.

Expt. 162. **Qualitative demonstration of suspensoid and emulsoid flocculation**—Pour 50 c.c. of an As_2S_3 sol into an Erlenmeyer flask. Add 50 c.c. of a clear egg-white solution to a second flask. The egg white may be prepared by diluting the fresh product 5 times with a 0.7 per cent. NaCl solution or by using a 2 per cent. solution of dried albumin in a 0.7 per cent NaCl solution. Add 5 drops of a saturated solution of ammonium sulphate to the As_2S_3 sol and turbidity results immediately. A similar addition to the egg white produces no turbidity. A large amount, such as 20–30 c.c. of ammonium sulphate solution, will produce turbidity and finally flocculation.

Certain electrolytes separate the water of hydration from the colloid particles. This is a specific property of individual salts and for which general rules are not yet known. The aggregation and condensation of the dehydrated colloid particles in an aqueous dispersion medium involve electrical and electrochemical factors. The electrical charge plays just as important a rôle in emulsoids as in suspensoids. Electrically neutral albumin sols, such as serum albumins, are flocculated by neutral salts, alcohol, etc. (Wo. Pauli).

The electrolytic flocculation of albumin sols, previously studied, show complex relations. The following generalizations have been established. There are two large classes of albumin sols, the isostable and isolabile albumin sols.

Isostable albumin sols are stable at the "isoelectric points," that is, in a state of complete electrical neutrality. Serum and egg albumin, hæmoglobin, gelatin belong in this class. Isolabile albumin sols, when in a state of electrical neutrality, are no longer colloiddally soluble and hence flocculate. Such sols are globulin, casein, stable in weakly acid or alkaline solutions.¹ Albumin sols are usually amphoteric, that is, they may be either positively or negatively charged, depending upon certain conditions. They are more easily charged than suspensoids by the addition of a small amount of alkali or acid. In alkaline media the sol is negatively charged, while in acid media it is positively charged. The behaviour of these sols is in some respects similar to suspensoid sols. The differences between these sols is that the absolute precipitation values of these emulsoids are smaller; the influence of oppositely charged ions is more pronounced and flocculation is partly reversible. While the neutral emulsoids (genuine albumin) show the Hofmeister series, especially the cation series, rather indefinitely by flocculation experiments, the charged protein sols definitely show the series (R. Höber). The Hofmeister series is reversible, depending upon an alkaline (negative) or acid (positive) sol medium.

Expt. 163. Acid and alkaline flocculation of casein sol (an isolabile albumin sol)—Add 3–5 g. of powdered casein to 100 c.c. of a 0.01N NaOH solution, shake the mixture repeatedly, and allow to stand for 24 hours. The saturated casein sol freed from undissolved casein by filtering, shows a very weak alkaline reaction towards phenolphthalein. Pipette 2 c.c. of the casein sol into a series of test-tubes and determine in the usual

¹ The former protein sol corresponds in behaviour to the sulphide sols, while the serum albumin behaves like silicic acid sol in inorganic systems.

manner the concentration of HCl and NaOH at which the sol becomes turbid or flocculates. Start with 0.01N HCl and gradually decrease the concentration. The first acid flocculation of the sol occurs with a mixture of 2 c.c. of casein sol and 3.0 c.c. 0.01N HCl + 5 c.c. H₂O. This acid flocculation value is equivalent to about **0.0025** mols. The isoelectric point is attained at this concentration. According to L. Michaelis, the (H⁺)-ion concentration of the isoelectric point is equal to $2-4 \times 10^{-5}$. A second flocculation occurs with higher acid and alkali concentrations. The flocculating concentrations for HCl is about **0.25** mols, i.e. about 100 times greater concentration of acid than that required for the first flocculation point, and for NaOH it is about 5 mols. These flocculation values may be determined more accurately by starting with N HCl in one case and with 8N NaOH in the other.

Expt. 164. **Neutral salt flocculation of hæmoglobin** (an isostable albumin sol)¹—Use the powdered preparation; if the hæmoglobin is in the form of lamellæ, grind it in a mortar before use. Dissolve 2 g. in 100 c.c. of water by first grinding the powder with a little water in the mortar in order to lessen lump formation. A better method is to sift the powder by brushing it through a wire screen into a beaker containing water constantly stirred. Filter the solution and proceed as in the previously described flocculation experiments by pipetting

¹ In the experience of the author, coagulation experiments on hæmoglobin are particularly suited for this important chapter on the colloid chemistry of proteins. The material is easily obtainable in uniform composition; it gives relatively clear solutions of greater concentration than serum or egg albumin; it may be dissolved in any desired concentration and acidified or made faintly alkaline without inducing coagulation. The flocculation value is relatively low, so that working with extremely concentrated acid solutions or with salts is obviated. The flocculation value may be determined with great accuracy.

2 c.c. of the hæmoglobin solution into a series of test-tubes. Prepare the salt mixtures in another series of tubes and make them up to a volume of 8 c.c. Thorough mixing may be obtained by pouring the added solutions back and forth several times. The point at which a distinct turbidity is observed immediately after mixing may be taken as the flocculation concentration. Turbidity is recognized by comparing with a control tube. Determine the flocculation values of a number of electrolytes on the neutral, weakly alkaline and weakly acid hæmoglobin solutions. The following example gives the approximate flocculation values usually obtained :¹

I. ELECTROLYTIC FLOCCULATION OF HÆMOGLOBIN

K_3 -citrate, 2N = 0.66 mols.

$$2 \text{ c.c. hæm. } + [2 \text{ c.c. } K_3\text{-citrate} + 6 \text{ c.c. } H_2O] = 0.134 \text{ molar}$$

$$2 \text{ c.c. hæm. } + [4 \text{ c.c. } K_3\text{-citrate} + 4 \text{ c.c. } H_2O] = 0.267 \text{ molar}$$

$K_2 SO_4$, 1N = 0.5 molar.

$$2 \text{ c.c. hæm. } + [4 \text{ c.c. } K_2SO_4 + 4 \text{ c.c. } H_2O] = 0.2 \text{ molar}$$

$$2 \text{ c.c. hæm. } + [8 \text{ c.c. } K_2SO_4 + 0 \text{ c.c. } H_2O] = 0.4 \text{ molar}$$

K-acetate, 2N = 2 molar.

$$2 \text{ c.c. hæm. } + [2 \text{ c.c. K-acetate} + 6 \text{ c.c. } H_2O] = 0.4 \text{ molar}$$

$$2 \text{ c.c. hæm. } + [4 \text{ c.c. K-acetate} + 4 \text{ c.c. } H_2O] = 0.8 \text{ molar}$$

¹ In the author's knowledge, previous investigations on the neutral salt flocculation of hæmoglobin are as yet not available. In the above experiment the heavy-typed figures are only approximate flocculation values,

KCl, 4N = 4 molar = saturated.

2 c.c. hæm. + [4 c.c. KCl + 4 c.c. H₂O] = 1.6 molar

2 c.c. hæm. + [6 c.c. KCl + 2 c.c. H₂O] = 2.4 molar

2 c.c. hæm. + [8 c.c. KCl + 0 c.c. H₂O] = 3.2 molar

KNO₃, 4N = 4 molar = saturated.

2 c.c. hæm. + 8 c.c. KNO₃ = 3.2 molar.

Flocculation value > 3.2 molar

KCNS, saturated = ca. 14 molar ; no flocculation.

For three additional sulphates and chlorides, the following flocculation values are shown in a similar manner :

(NH₄)₂SO₄ = 0.09 molar CaCl₂ = 0.004 molar

Na₂SO₄ = 0.8 ,, MgCl₂ = 0.004 ,,

Li₂SO₄ = 2.0 ,, AlCl₃ = > 2.4 ,,

Arrange in series the flocculation values obtained for the potassium salts : citrate, sulphate, acetate, chloride, nitrate, sulphocyanide. The cations with the sulphates give the series : NH₄, K, Na, Li. The chlorides of the alkaline earths show extraordinarily small flocculation values.

II. FLOCCULATION OF ELECTRONEGATIVE HÆMOGLOBIN

Final concentration = 0.03N NaOH.

2 c.c. hæm. + [2 c.c. saturated = ca. 4 molar (NH₄)₂SO₄ + 6 c.c. H₂O + 6 drops 1N NaOH] = 0.8 molar, immediate flocculation.

2 c.c. hæm. + [8 c.c. saturated = ca. 8 molar NH₄CNS + 6 drops 1N NaOH] = ca. 6 molar ; no flocculation.

III. FLOCCULATION OF ELECTROPOSITIVE HÆMOGLOBIN

2 c.c. hæm. + [2 c.c. molar (NH₄)₂SO₄ + 6 c.c. H₂O + 6 drops NH₄Cl] = 0.2 molar ; immediate flocculation.

2 c.c. hæm. + [2 c.c. 0.2 molar NH_4CNS + 6 c.c. H_2O + 6 drops NHCl] = 0.04 molar ; immediate flocculation.

The experiments with alkaline and acid hæmoglobin give the following flocculation values : Negative sols—sulphate, 0.8 ; sulphocyanide, > 6.0 . Positive sols—sulphate, 0.8 ; sulphocyanide, 0.04. The sulphate flocculates negative sols more readily than sulphocyanide. However, the sulphocyanide reacts more strongly than the sulphate toward positive sols. These results show a reversal of the Hofmeister series, depending on the sign of the charged sols. Compare the behaviour of As_2S_3 and $\text{Fe}(\text{OH})_3$ [Expts. 140 and 141]. Determine the flocculation values of the above series, using 0.03N alkaline and acid solutions.

The following table is a summary of the flocculation values found by F. Hofmeister for egg white with potassium and sodium salts ¹:—

FLOCCULATION VALUES.

	Hæmoglobin (K-salts). Mols per litre.	Egg white (Na-salts). Mols per litre.
Citrate	0.27	0.56
Tartrate	—	0.78
Sulphate	0.4	0.80
Acetate	0.8	1.69
Chloride	2.4	3.62
Nitrate	> 3.2	5.42
Chlorate	—	5.52
Iodide	ca. 5	very large
Sulphocyanide	> 14	very large

¹ Cited after R. Höber, *Physical Chemistry of Cells*, 4th Edition, 1914, p. 308.

Determine the cation series, $\text{SO}_4^{=}$ as anion, with alkaline and acid hæmoglobin in the same way. The series obtained is as follows :

Alkaline Li^+ (1 mol) $>$ NH_4^+ (0.8) $>$ K^+ (0.5).

Acid Li^+ (0.13 mols) — NH_4^+ (0.04) — K^+ (0.025).

A greater sensitivity is shown by the acid sols, yet the cation series remains the same with the alkali and acid concentrations used. This does not apply to other concentrations of acid or alkali.

Concentrated hæmoglobin solutions are also flocculated by additions of acid or alkali mixed with neutral salts.

Expt. 165. “ **Irregular series** ” with dialysed egg white—Use an albumin sol freed from globulin and salts by dialysis. Prepare by the above procedure 2 c.c. of albumin and 8 c.c. of aqueous salt solution, using molal lead nitrate as follows :

2 c.c. albumin + 8 c.c. M $\text{Pb}(\text{NO}_3)_2 = 0.8$ molar.

2 c.c. albumin + [4 c.c. M $\text{Pb}(\text{NO}_3)_2 + 4$ c.c. H_2O]
= 0.4 molar, etc.

An experiment in which an old dialysed preparation was used, gave the following results after two hours :

0.8 molar	↑ strong flocculation	6.4 millimols	} clear
0.4 „		3.2 „	
0.2 „		1.6 „	weakly turbid
0.1 „	turbid	0.8 „	turbid
0.05 „	} clear	0.4 „	weakly turbid
0.025 „		0.2 „	} clear
0.0125 „		0.1 „	

Expt. 166. **Influence of temperature on the electrolytic flocculation of gelatin solutions**—Add enough saturated ammonium sulphate solution to 50 c.c. of 0.5–1 per cent. aqueous gelatin at room temperature until the first appearance of a faint turbidity. Clear the solution by adding a few drops of water. Pour the

mixture into three test-tubes. Place the first in an oven, the second in an ice-chest and allow the third to remain at room temperature. After 24 hours, the solution at the higher temperature has remained clear. A faint turbidity appears in the one at room temperature and a strong turbidity or flocculation in the tube which was placed in the ice-chest. If solutions 2 and 3 are warmed, the flaky precipitate dissolves to produce a slightly turbid liquid, which precipitates again on cooling. Compare with Expt. 159 on Congo rubin.

Expt. 167. **Flocculation of hydrated globulin by electrolytic extraction**—Egg white, next to albumin, contains considerable globulin. Globulin, like many suspensoids, is colloiddally soluble in the presence of certain small amounts of electrolyte. Not only (H^+) and (OH^-) ions, but particularly neutral salts have a dispersing action upon globulin. Prepare the following mixtures of natural egg white and distilled water:

5	c.c. egg white	+	5	c.c. H_2O
2.5	c.c. „	„	+ 7.5	c.c. „
1.25	c.c. „	„	+ 8.75	c.c. „
0.6	c.c. „	„	+ 9.4	c.c. „

Observe that increasing dilution produces a constantly increasing turbidity, and if the solution is diluted ten times, practically all the globulin precipitates.

Pour a few c.c. of fresh clear egg white into an analytic dialyser enclosed in a vessel. Guard against bacterial growth by adding chloroform. Dialyse for 1–2 days and change the water often. Large globulin aggregates appear within the dialyser. Compare analogous experiments with $Fe(OH)_3$ (Expt. 160).

Expt. 168. **Reversible and irreversible electrolytic flocculation of egg white**—Flocculate a mixture of 2 c.c. of egg white and 8 c.c. of salt solution with

ammonium sulphate (about one molar) and with calcium chloride. Allow the precipitate to settle, wash by decantation with distilled water or pour a few drops of the turbid mixture into a beaker containing distilled water. The ammonium sulphate precipitate redissolves, while barium, calcium and strontium salts, but not magnesium salts, produce irreversible flocculation (Wo. Pauli). Analogous to the suspensoid flocculation, reversibility or irreversibility of the process depends less upon the nature of the colloid and more upon the flocculating medium.

If the albumin receives a charge by addition of acid or alkali, then the flocculation by ordinary alkali salts becomes irreversible. Repeat the above experiment with ammonium sulphate, using a faintly acid and faintly alkaline albumin successively and observe that on longer standing, the flocculation becomes increasingly irreversible.

Expt. 169. **Alcohol flocculation of hæmoglobin**—Determine the flocculation value of ethyl alcohol upon neutral hæmoglobin. Use 2 c.c. of 2 per cent. hæmoglobin and 8 c.c. of alcohol-water mixture. The flocculation values are usually between 20 per cent. and 40 per cent. by volume of alcohol. Perform the same experiment with weakly acid (0.03N) and weakly alkaline (0.03N) hæmoglobin. Observe that the electrically charged hæmoglobin, which is strongly hydrated, may be flocculated by a rather high alcohol concentration.

COAGULATION OF DIALYSED EGG WHITE BY HEAT

The coagulation of albuminous substances by heat involves chemical changes of denaturization which accompany phenomena of flocculation. The chemical and colloidal processes may be differentiated from one another in such a way that under certain conditions the albumin

may be denaturized by heating without any flocculation resulting. However, the colloidal process of flocculation may be produced by cooling (Wo. Pauli and H. Handowsky).

Expt. 170. **Coagulation of dialysed egg white plus KCNS by heat**—Dialyse an egg-white solution from globulin and salts.¹ To the dialysed egg white add sufficient potassium sulphocyanide to make the solution approximately 2N and boil a few minutes. Allow to cool, pour half the mixture into an analytic dialyser and change the wash water frequently during the first hour. Usually, a strong turbidity appears in the dialyser after a few hours, while the undialysed mixture has remained clear. The same results may be obtained by using KI instead of KCNS. Denaturization rather than flocculation results in the presence of sulphocyanide. Flocculation may be produced by the removal of this salt. This is analogous to the flocculation of globulin by dialysis of natural egg white.

Expt. 171. **Influence of electrolytes on the coagulation temperature of dialysed egg white**—The simplest method for the determination of coagulation temperature is the optical method based upon the appearance of turbidity (see page 132). The coagulation temperature depends upon the rate of heating, as in the experiments upon gelation, corresponding to Expt. 108. A larger "normal" rate of temperature change, 1° C. per minute, is advisable for this experiment. The solutions are conveniently heated in a small test-tube placed in a beaker of water. The results may be reproduced accurately to at least half a degree, after a few trials.

Determine the coagulation temperature in the presence of neutral salts, such as the potassium salt used in Expt.

¹ The above experiment cannot be performed with non-dialysed globulin containing egg white.

153, with a final concentration of 0.5, 0.25 and 0.125N. The following example gives approximate values¹:

no addition	60°	nitrate	65°
citrate	78°	bromide	62.5°
acetate	78°	iodide	60°
chloride	67°	sulphocyanide	60°

Observe that all salts which exert any influence raise the coagulation temperature (Wo. Pauli).² Furthermore, the Hofmeister series appears again. R. Höber finds a reversal of the Hofmeister series on using similar concentrations with dialysed egg white³:

acetate	62.0	bromide	66.5
chloride	62.0	iodide	76.5
nitrate	66.4	sulphocyanide	77.2

Other salt concentrations produce an irregularity in the series so that with egg white and 0.15N mixtures a reversal of the ionic series occurs (R. Höber). Using concentrations of iodide, cyanide, sulphocyanide, etc., and raising the temperature produces no flocculation.

Expt. 172. **Theory of emulsoid precipitation**—Emulsoids are liquid-liquid systems. The following experiment proves the applicability of this definition (K. Spiro, Wo. Pauli). Mix a hot 5 per cent. gelatin solution with sufficient powdered sodium sulphate, such as 2–2.5 M solution, to form a milky flocculate. Place the test-tube containing the gelatin-salt mixture upright in an incubator or water-bath. Heat at a temperature of 35°–50° C. for 24 hours. The precipitate settles, but on account of its high water content at the above temperature it flows into a completely coherent yellow layer,

¹ An old preparation preserved in toluol was used.

² All salts decrease the turbidity of gelatin solutions according to Expt. 84.

³ R. Höber, Hofmeister's *Beiträge*, **11**, 51 (1907).

which is often clear and at least transparent at the edges. The precipitate behaves like a fluid when the vessel is tipped. The disperse phase is still a liquid under the experimental conditions described.

A liquid gel may be obtained more rapidly if a 1-2 per cent. gelatin solution is flocculated with 0.5N salicylic acid and allowed to stand for 30 minutes at 35°-40° C. The precipitate, depending upon the amount flocculated, settles to the bottom of the tube in the form of drops or as a coherent phase.

There is no doubt that a part of the neutral salt action consists in a dehydration of the colloid particles. Therefore the disperse phase of the colloid in the above experiment is richer in water when uncoagulated and must have the properties of liquid drops.

C. OPPOSING INFLUENCE OF COLLOIDAL SOLUTIONS

I. FLOCCULATION OF TWO COLLOIDS

Hardy's rule states that oppositely charged colloid particles flocculate each other. This is also true of coarsely disperse, colloidal, or molecularly disperse particles of opposite charges. Flocculation of two oppositely charged colloids may be simultaneously produced by mixing them. This type of flocculation is characterized by the fact that it may occur only when the ratio of the concentrations of the two colloidal solutions lies within certain narrow limits. Often many trials must be made in performing such experiments before optimum flocculation concentrations are found. Such concentrations produce a completely clear supernatant liquid, due to complete flocculation. Prepare a dozen mixtures of night blue and Congo red at optional concentrations and record

the proportions. A systematic procedure must be used for the determination of flocculation optima.

Reciprocal flocculation of colloids may often be regarded as reciprocal adsorptions. The precipitates formed are a particularly important class of adsorption compounds. These precipitates differ from ordinary chemical precipitates in that their components are not necessarily combined in stoichiometrical proportions (compare Expts. 178 and 179).

Expt. 173. **Reciprocal flocculation of arsenic trisulphide and ferric hydroxide sols**—Prepare an As_2S_3 sol from 0.5 per cent. As_2O_3 according to Expt. 153 and dialysed ferric hydroxide by Graham's method. The flocculation optimum may easily be found when using such sol mixtures. The following table gives a personally conducted experiment. The results were noted after 24 hours.

As_2S_3 sol; content 0.5 per cent. referred to As_2O_3 .

$\text{Fe}(\text{OH})_2$ sol; content 0.5 per cent. referred to Fe_2O_3 .

1	c.c. As_2S_3	+	9	c.c. $\text{Fe}(\text{OH})_2$	clear brown
2.5	„	„	+ 7.5	„	faintly turbid
5.0	„	„	+ 5.0	„	turbid
7.5	„	„	+ 2.5	„	precipitate, turbid, brown supernatant liquid
9.0	„	„	+ 1.0	„	completely flocculated, clear colourless supernatant liquid
9.5	„	„	+ 10 drops	„	precipitate, turbid, yellow supernatant liquid
10	„	„	+ 5	„	precipitate, faintly turbid, yellow supernatant liquid

10 c.c. As_2S_3 + 2 c.c. $\text{Fe}(\text{OH})_3$ fine precipitate
 10 „ „ + 1 „ „ clear yellow.

Expt. 174. **Reciprocal flocculation of Congo red¹ and night blue** (Buxton and Teague)—Prepare the following four solutions of Congo red and the following eight solutions of night blue, starting from 1 per cent. solutions :

Congo red : 0·0125, 0·0100, 0·0083, 0·0063 per cent.
 Night blue : 0·0333, 0·0250, 0·0200, 0·0167 per cent.
 0·0125, 0·0100, 0·0083, 0·0063 per cent.

5 c.c. of Congo red are mixed with 5 c.c. of night blue according to the following scheme :—

Congo red.	Night blue.				
0·0125	0·0333	0·0250	0·0200	0·0167	0·0125
100	0·0250	0·0200	0·0167	0·0125	0·0100
83	0·0200	0·0167	0·0125	0·0100	0·0083
63	0·0167	0·0125	0·0100	0·0083	0·0063

In an example personally conducted, complete flocculation resulted and a colourless supernatant liquid appeared. The optimum quantities necessary for flocculation usually vary with the salt content of the individual sols.

Expt. 175. **Reciprocal titration of two dyes** (L. Pelet-Jolivet)—The previous experiment may be modified and performed quicker by using Tüpfel's method. Place a drop of both dyes mixed in proportions insufficient for complete flocculation upon filter paper. The dye present in excess forms a "mirror." If the Congo red is in excess, the mirror or its edge is red. If the night blue is in excess, the edge is blue. Two reciprocally

¹ Not to be confused with Congo rubin.

flocculating dyes may be titrated by the Tüpfel method described by L. Pelet-Jolivet, *The Theory of Dyeing*, p. 49 (Dresden, 1910). The following experiment conducted by the author is illustrative:

5 c.c. 0.01 per cent. Congo red titrated with 0.033 per cent. night blue.

3.0 c.c.	night blue,	red mirror.
5.0 c.c.	„	same, but weaker.
6.0 c.c.	„	much weaker.
6.2 c.c.	„	indifferent mirror.
6.5 c.c.	„	faint blue mirror.
7.0 c.c.	„	decided blue mirror.

The proportional amounts in this example are 6.2 parts of night blue to 5 parts Congo red, equal to 1.24. When titrating 5 c.c. of 0.0063 per cent. Congo red with 0.33 per cent. night blue, the proportions amount to 61 parts of night blue to 38 parts Congo red or 1.22. In a great number of experiments carried out in the laboratory, 5 c.c. of 0.01 per cent. Congo red, titrated with 0.01 per cent. night blue in a porcelain dish with a glass rod, gave a proportion 1.2 to 1.3. When titrating with more dilute mixtures, a value of about two is obtained. The amounts by weight necessary for complete reciprocal adsorption are independent of the concentration of the reaction mixture. A convenient pair of dyes is methylene blue and crystal ponceau.

II. PROTECTIVE ACTION

M. Faraday discovered that small amounts of solvated emulsoids bestow a considerably greater stability upon suspensoids toward the flocculating action of electrolytes. The action of such protective colloids was already men-

tioned in the preparation of colloidal solutions (Expts. 45 and 46). Their mode of action is not due to an increase in the viscosity of the dispersion medium, for in many cases very small amounts prove effective. There appears to be a union between the suspensoid and emulsoid particles, with the result that the relative stability of the protective colloid is decisive for the whole complex. As yet it is not known if there is "coating" or "enveloping" of the suspensoid particle by the liquid drops of the protective colloid.

Such protective colloids are gelatin, isinglass, albumin, casein, hæmoglobin, tragacanth, acid and alkaline hydrolysis products of egg white, lysalbin and protalbin acids, tannin, etc. Freshly prepared stannic acid is a protective inorganic colloid. Related material in regard to organic protective colloids may be obtained from the studies of A. Gutbier and his students in the *Kolloid. Zeitschrift*, 1916-1922.

Expt. 176. **Gold numbers** (R. Zsigmondy)—Use an electrolyte-sensitive red gold sol, prepared in Expt. 3 with alcohol. [R. Zsigmondy, *Colloid Chemistry*, 2nd edition, 1918, p. 174; *Zeitschr. f. analyt. Chem.*, **40**, 697 (1901).] Place 0.01, 0.1, 1.0, etc., c.c. of the protective colloid to be studied in a series of small beakers with just 10 c.c. of a red electrolyte-sensitive gold sol. After 3 minutes, pour 1 c.c. of a 10 per cent. solution of NaCl into each beaker, with constant shaking. By systematic decreasing of the limits of concentration determine which concentration of protective colloid is just sufficient to prevent the sudden colour change from red to blue. These numbers expressed according to R. Zsigmondy in mg. of protective colloid, may be more conveniently expressed in per cent. and are known as the "gold numbers" of the protective colloids used. The orders of magnitude are:

Gelatin	0.00005–0.0001 per cent.
Oxyhæmoglobin	0.0003–0.0007 per cent.
Sodium caseinate	0.0001 per cent.
Albumin	0.001–0.002 per cent.
Starch	ca. 0.25 per cent.

The gold numbers give a quantitative estimate of the protective power of various emulsoids. They may only be taken as relative and not as absolute values because their numerical values vary not only according to the nature of the gold sol, such as degree of dispersion, concentration, mode of preparation, etc., but also with the colloidal nature of the protective colloid. Determine the silver number in a similar manner by using a brown-red sol, prepared in Expt. 10, and choose for the end point its sudden change to grey-violet. Determine the As_2S_3 number by assuming at the end point the appearance of turbidity upon mixing.

Expt. 177. “**Congo-rubin numbers**”—Congo rubin is also suitable for the quantitative study of protective action and may be used as a gold sol substitute. Start with a 1 per cent. dye solution and pipette 1 c.c. into small test-tubes or beakers. Add various amounts of the protective colloid solution to the Congo rubin, make up to a volume of 5 c.c. with water and add to each mixture 5 c.c. of 0.5N KCl. Determine the concentration of protective colloid, which produces a difference in colour shade after ten minutes. Compare with a control solution containing KCl of the same concentration. The following “Congo rubin numbers” are illustrative :

Sodium caseinate	0.004 per cent.
Hæmoglobin	0.008 per cent.
Albumin	0.020 per cent.
Gelatin	0.025 per cent.
Soluble starch	ca. 0.1 per cent.
Starch	ca. 0.2 per cent.

Expt. 178. **Cassius purple**—Add a few c.c. of a 0.01 per cent. solution of stannous chloride to a 0.05 gold chloride solution. A brown to a beautiful purple-red colour first appears and the sol flocculates upon addition of any neutral salt. This so-called Cassius purple is an “adsorption” compound of colloidal gold and colloidal stannic acid. Such a composition was predicted by M. Faraday. As in the preparation of tannin gold (Expt. 2), the addition of stannous chloride acts in two ways: (1) It produces colloidal gold by reduction; (2) the colloidal stannic acid, formed by hydrolysis at such a dilution, acts as a protective colloid.

The correctness of this assertion is shown by the fact, as pointed out by R. Zsigmondy, that if separately prepared solutions of colloidal gold and stannic acid are mixed, the resulting mixture behaves like Cassius purple. Add to a red gold sol a stannic acid sol prepared from stannous chloride, according to Expt. 39, and then a neutral salt to the solution. Compare with a similar experiment, using a pure gold sol. The gold-stannic acid mixture does not change suddenly to blue-violet. This mixture illustrates the colloidal reaction of stannic acid sols, since a coarse rather than a fine red precipitate is formed. Old preparations of stannic acid sometimes show a rather weak protective action.

Analogous adsorption compounds may be prepared with colloidal silver or platinum and stannic acid.

Expt. 179. **Rubin purple**—The protective action of stannic acid may be shown with Congo rubin as well as with gold sol. Add 2–3 c.c. of a stannic acid sol, prepared in Expt. 39, to 10 c.c. of a 0.01 per cent. Congo-rubin solution, freshly prepared with CO_2 free distilled water.¹ Add the same amount of water to a control solution.

¹ The amounts added vary with the concentration of the stannic acid sol and can be determined in advance.

The control suddenly changes to a deep blue or violet in a few seconds. Addition of neutral salts causes the most rapid and complete change, especially upon addition of a few drops of 0.01N aluminium sulphate. The sol protected with stannic acid remains red. It is difficult to prepare mixtures containing a strong excess of salt which will remain distinctly red after standing a few hours, for a red precipitate gradually separates out. The precipitate, rubin purple, is an analogue to Cassius purple.

D. PEPTIZATION

Peptization is the reverse of coagulation. It involves a change of a coarsely disperse precipitate into the colloidal state. Examples of peptization were given in Expts. 30-39. In the simplest cases the precipitate spontaneously decomposes to form the colloidal solution. In other cases the precipitate may be changed into a colloid by dilution or washing. This is known as reversible colloidal solubility and has already been mentioned in the paragraph preceding Expt. 30. Such examples represent peptization processes in a restricted sense and generally consist in the treatment of precipitates with electrolyte solutions. Examples were given in Expts. 30-39; other peptization processes are described in the following experiments.

Expt. 180. **Peptization phenomena**—Flocculate a ferric hydroxide sol prepared by the Graham method with potassium citrate by first preparing a whole series of concentrations in order to determine the flocculation optimum.¹ Decant or wash the gel by centrifuging and mix the gel with a little ammonium hydroxide to change it into a colloidal solution.

¹ The flocculation of ferric hydroxide sol with citrate gives an irregular series.

Flocculate a large amount of silver sol with ammonium nitrate and wash the precipitate as above. Suspend it in distilled water to which a trace of NH_4OH has been added. The precipitate regains its colloidal state, giving a clear brownish stable gel. Wash the purple of Cassius obtained by precipitating a red gold sol with potassium chloride and suspend it in water. Upon addition of small amounts of NH_4OH , a colloidal solution is obtained. The same experiment may be performed with rubin purple.

Colloidally disperse substances are acted on by the same reagents that combine chemically with the substances in a coarser state. Hence, chemical changes in colloid solutions which lead to molecular dispersion are called dissolutions. It appears, however, that such dissolution is modified in some respects by the colloid state.

Expt. 181. **Dissolution of red gold sols by potassium cyanide** (C. Paal)—Add a few drops of 2N potassium cyanide solution to a gold sol. The gold, upon gentle warming, instantaneously decolorizes or will do so within five minutes at room temperature.

The experiment at the same time furnishes an example of the increased rate of reaction of colloid systems according to the so-called Wenzel law. If a larger piece of gold is left in contact with KCN, a small amount dissolves after some time; hence the rate of dissolution is slower.

Expt. 182. **Behaviour of silver sols toward nitric acid**—Mix a suitably concentrated brown-red silver sol with a few drops of nitric acid. The sol changes to a grey-violet or black and then flocculates. It gradually dissolves after continued shaking and standing.

Expt. 183. **Coagulation and dissolution of silver bromide sols by ammonium hydroxide** (R. Auerbach)

—Prepare a fresh silver bromide sol in the following way : Add 12 c.c. of 0.1N KBr to 80 c.c. of distilled water and add 8 c.c. of 0.1N AgNO_3 solution. Pour 10 c.c. into four test-tubes, add the following quantities of solution and stir :

- Tube 1. 10 c.c. distilled water.
,, 2. 2.5 c.c. 2N NH_4OH + 25 c.c. distilled water.
,, 3. 10 c.c. 2N NH_4OH .
,, 4. 10 c.c. 4N or stronger NH_4OH .

Tube 1 serves as a control. Immediately after the addition to tube 2 a stronger turbidity appears. The solution in tube 3 increases in turbidity and then becomes clear. Dissolution takes place instantaneously in tube 4.

The question whether a sol first flocculates upon addition of a dissolving electrolyte or is directly dissolved is obviously answered by comparing the rates of both processes. The rate of flocculation of silver sol is greater than that of dissolution. Mix an As_2S_3 sol with NaOH or a positive $\text{Fe}(\text{OH})_3$ sol with a little HCl. The dissolution process proceeds so rapidly that flocculation by this addition of electrolyte is apparently impossible, at least it cannot be observed. The addition of larger amounts of HCl to a $\text{Fe}(\text{OH})_3$ sol first causes a flocculation. The silver bromide experiment illustrates these three possibilities.

IX

COMMERCIAL COLLOIDS

THERE are numerous commercial "natural" colloids. Hydrated emulsoids are, as a rule, obtainable as solid resolvable gels. They may be used for colloid chemistry experiments in this state, as well as in the disperse form, in a suitable dispersion medium. Suspensoids are likewise prepared in a solid resolvable form. The sols made by electrical methods are obtainable in solution.

A. INORGANIC COMMERCIAL COLLOIDS

METAL COLLOIDS¹

GOLD

Colloidal gold—Dark red glistening lamellæ. Colour of solution : reddish black, metallic ; purple red in transmitted light. Au content, about 75 per cent.

Electro-colloidal gold solution—Colour of solution : reddish black in reflected light ; violet red in transmitted light. Au content, about 0.03 per cent.

Colloidal gold solution—Colour of solution : dark

¹ The number of colloid particles is proportional to the strength of the current. The base metals formed in aqueous solution undoubtedly have oxidation products in addition to the metallic element.

red in reflected light ; purple red in transmitted light.
Au content, about 0.005 per cent.

PLATINUM, PALLADIUM

Colloidal platinum—Black glistening lamellæ. Colour of solution : deep black in reflected light ; deep brown in transmitted light. Pt content, about 60 per cent.

Electro-colloidal platinum solution—Colour of solution : black in reflected light ; dark brown in transmitted light. Pt content, about 0.04 per cent.

Electro-colloidal palladium—Colour of solution : greenish brown. Pd content, about 0.08 per cent.

SILVER

Collargol—Metallic glistening, brown green lamellæ. Colour of solution : black brown in reflected light ; dark brown in transmitted light. Ag content, about 75 per cent.

Electro-collargol—Colour of solution : black brown in reflected light ; dark brown in transmitted light. Ag content, 0.06 per cent.

Electro - collargol, concentrated — Ten times stronger than the previous solution. Colour of solution : deep black in reflected light ; dark brown in transmitted light. Ag content, 0.6 per cent.

Skiargan—A 10 per cent. sterile solution of a stable 90 per cent. colloidal silver. It is used for Röntgen diagnosis, especially in pyelography. Ag content, 9 per cent.

Choleval is a colloidal silver with gallic acid salts as a protective colloid.

MERCURY

Colloidal mercury—Heavy grey black; external surface of particles show metallic lustre. Colour of solution: grey black in reflected light; deep brown in transmitted light. Hg content, about 7 per cent.

Electro-colloidal mercury—Solid, grey black, shining, heavy particles. Colour of solution: grey in reflected light; light grey brown in transmitted light. Hg content, about 55 per cent.

Electro-colloidal mercury solution—Colour of solution: grey in reflected light; brown in transmitted light. Hg content, about 0.09 per cent.

COPPER

Electro-colloidal copper—Colour of solution: black in reflected light; dark reddish brown in transmitted light. Cu content, about 0.22 per cent.

ARSENIC

Colloidal arsenic—Blue black glistening lamellæ. Colour of solution: reddish brown to grey in reflected light; dark reddish brown in transmitted light. As content, about 33 per cent.

ANTIMONY

Colloidal antimony—Black glistening lamellæ. Colour of solution: grey black in reflected light; dark reddish brown in transmitted light. Sb content, about 20 per cent.

·VANADIUM

Colloidal vanadium—Colour of solution: grey black in reflected light; greenish grey in transmitted light. V content, about 0.07 per cent.

TIN

Electro-colloidal tin—Colour of solution: grey black in reflected light; grey brown in transmitted light. Sn content, about 0.3 per cent.

TITANIUM

Electro-colloidal titanium solution—Colour of solution: grey green in reflected light; brown green in transmitted light. Ti content, about 0.6 per cent.

LEAD

Electro-colloidal lead solution—Colour of solution: grey black in reflected light; dark brown in transmitted light. Pb content, about 0.11 per cent.

NICKEL

Electro-colloidal nickel solution—Colour of solution: black in reflected light; brownish green in transmitted light. Ni content, about 0.05 per cent.

COBALT

Electro-colloidal cobalt solution—Colour of solution: deep black brown in reflected light; dark brown in transmitted light. Co content, about 0.03 per cent.

CADMIUM

Electro-colloidal cadmium solution—Colour of solution : grey in reflected light ; dark brown in transmitted light. Cd content, about 0.03 per cent.

IRON ¹

Colloidal iron—Dark red lamellæ or red powder. Colour of solution : red. Fe content, about 12–13 per cent.

Electro-colloidal iron solution—Colour of solution : black in reflected light ; dark reddish brown in transmitted light. Fe content, 0.5 per cent.

CHROMIUM

Electro-colloidal chromium—Colour of solution : reddish grey in reflected light ; dark reddish brown in transmitted light.

MANGANESE

Colloidal manganese—Black glistening lamellæ or grey powder. Colour of solution : dark red brown in reflected light ; light grey in transmitted light. Mn content, about 12 per cent.

MOLYBDENUM

Electro-colloidal molybdenum—Colour of solution : black brown in reflected light ; reddish brown in transmitted light. Mo content, about 0.04 per cent.

¹ Compare Note 1, p. 171.

TUNGSTEN

Electro-colloidal tungsten—Colour of solution : black in reflected light ; dark red brown in transmitted light. W content, about 0.033 per cent.

URANIUM

Electro-colloidal uranium—Colour of solution : grey black in reflected light ; dark brown in transmitted light. U content, about 0.1 per cent.

SULPHUR

Colloidal sulphur—Grey white powder. Colour of solution : milky white in reflected light ; bluish in transmitted light. S content, about 75 per cent.

Colloidal sulphur used for injections—Grey white lamellæ. Colour of solution : milky in reflected light ; reddish blue in transmitted light. S content, about 6 per cent.

SELENIUM

Colloidal selenium—Dark reddish brown heavy lamellæ. Colour of solution : brick red, turbid in reflected light ; blood red in transmitted light. Se content, about 52 per cent.

Electro-colloidal selenium—Colour of solution : brick red in reflected light ; blood red in transmitted light. Se content, about 0.01 per cent.

CARBON

Colloidal graphite with tannin as a protective colloid or with mineral oil as a dispersion medium. Electro-colloidal carbon is a brownish black liquid.

COLLOIDAL COMPOUNDS

MERCURIC SULPHIDE

Colloidal mercuric sulphide—Glistening lamellæ. Colour of solution: black in reflected light; brown black in transmitted light. HgS content, about 65 per cent.

ANTIMONY TRISULPHIDE

Colloidal antimony trisulphide—Red brown to grey green iridescent glistening lamellæ. Colour of solution: green and red in reflected light; blood red in transmitted light. Sb_2S_3 content, about 75–77 per cent.

ARSENIC TRISULPHIDE

Colloidal arsenic trisulphide—Yellowish brown lamellæ. Colour of solution: bright yellow in reflected light; dark yellow in transmitted light. As_2S_3 content, about 66 per cent.

SILVER SULPHIDE

Colloidal silver sulphide—Black and yellow lamellæ. Colour of solution: grey black in reflected light; brown black in transmitted light. Ag_2S content, about 35 per cent.

ZINC SULPHIDE

Colloidal zinc sulphide—Brown glistening lamellæ. Colour of solution: yellowish grey in reflected light; brownish yellow in transmitted light. ZnS content, about 20 per cent.

SILVER CHLORIDE

Colloidal silver chloride—Grey white glistening lamellæ. Colour of solution: milky white in reflected light; light brown in transmitted light. AgCl content, about 77 per cent.

SILVER BROMIDE

Colloidal silver bromide—Yellow glistening lamellæ. Colour of solution: grey yellow in reflected light; reddish brown in transmitted light. AgBr content, about 87 per cent.

SILVER IODIDE

Colloidal silver iodide—Yellow lamellæ. Colour of solution: milky yellow in reflected light; reddish yellow in transmitted light. Ag content, 31.7 per cent.; I content, about 37.3 per cent.

MERCUROUS CHLORIDE (CALOMEL)

Colloidal mercurous chloride—Greyish yellow powder. Colour of solution: milky grey in reflected light; brownish in transmitted light. Hg_2Cl_2 content, about 75 per cent.

MERCUROUS BROMIDE

Colloidal mercurous bromide—Yellow brown lamellæ. Colour of solution: milky grey in reflected light; brownish yellow in transmitted light. Hg_2Br_2 content, about 80 per cent.

MERCUROUS IODIDE

Colloidal mercurous iodide—Yellow brown lamellæ. Colour of solution: intense yellow in reflected light; orange yellow in transmitted light. Hg_2I_2 content, about 87–88 per cent.

FERRIC IODIDE

Colloidal ferric iodide—Colour of solution: black in reflected light; red brown in transmitted light. Fe_2I_6 content, about 0.5 per cent.

SILVER CHROMATE

Colloidal silver chromate—Reddish black glistening lamellæ. Colour of solution: brick red. $\text{Ag}_2\text{Cr}_2\text{O}_7$ content, about 70 per cent.

MERCUROUS CHROMATE

Colloidal mercurous chromate—Black, faintly glistening lamellæ. Colour of solution: grey green in reflected light; brown in transmitted light. Hg_2CrO_4 content, about 64 per cent.

FERRIC ARSENITE

Colloidal ferric arsenite—Ruby red, glistening lamellæ. Colour of solution: red in reflected light; orange red in transmitted light. Fe_2O_3 content, about 30.6 per cent.; As_2O_3 , about 35–39 per cent.

MERCURIC SALICYLATE

Colloidal mercuric salicylate—Grey yellow glistening lamellæ. Colour of solution : grey. Mercuric salicylate content, about 60 per cent.

FERRIC HYDROXIDE

The pharmaceutical dialysed ferric oxide in concentrations of 5 and 10 per cent. usually contains considerable amounts of chloride. Colour of solution : reddish black in reflected light ; red in transmitted light. Fe_2O_3 content, about 0.55 per cent.

ALUMINIUM HYDROXIDE

Colloidal aluminium hydroxide—Colour of solution : turbid to bluish. Al_2O_3 content, about 1 per cent. An interesting gel of aluminium is the so-called "native" alumina, according to H. Wislicenus.

SILICIC ACID

Very pure, neutral to litmus, silicic acid is produced commercially, such as the 2.6 per cent water-white solution used as a toxin adsorbent. The gel "osmosil" is a preparation which has a definite solubility in cold water. Another preparation is W. A. Patrick's silica gel. Colour of solution : a clear liquid. SiO_2 content, about 2 per cent.

ZINC OXIDE

Colloidal zinc oxide—Colour of solution : grey yellow in reflected light ; brownish yellow in transmitted light. ZnO content, 0.06 per cent.

MANGANESE PEROXIDE

Colloidal manganese peroxide—Black glistening lamellæ. Colour in solution: dark brown in reflected light; black in transmitted light. MnO_2 content, about 40 per cent.

Colloidal manganese peroxide solution—Colour of solution: black in reflected light; dark reddish brown in transmitted light. MnO_2 content, 2 per cent. solution of a 50 per cent. colloidal MnO_2 .

INORGANIC COLLOIDS WITH SOLID DISPERSION MEDIA

Gold ruby-glass—This is almost colourless or faint yellow. The gold cannot be recognized ultramicroscopically and therefore exists in a molecular disperse state. Other preparations are red to violet, blue by transmitted light and yellowish brown by reflected light. The latter is strongly turbid, containing aggregated gold.

Copper glass—Colloidal metallic copper is the colouring component according to R. Zsigmondy (*Kolloidchemie*, 2nd Edition, p. 109).

Silver glass—Yellow, red, violet, greenish, etc., colours, corresponding to increasing size of particle of the colloidal silver.

Selenium glass—Yellow, red, violet, etc., colours, corresponding to the size of the particles.

Colloidal colour media are present in other coloured glasses such as calcium fluoride in milk glass, chromium and iron compounds in green and violet glasses.

Colloidal sodium in rock salt—The coloration of blue rock salt is in all probability due to colloidal metallic sodium. Blue rock salt is prepared synthetically by heating colourless rock salt with metallic sodium.

B. ORGANIC COMMERCIAL COLLOIDS

The great abundance of organic gels may be brought into colloidal solution by treatment with a suitable dispersing medium.

Albuminous bodies and related compounds—Glue, gelatin, isinglass, dried egg and serum albumin, hæmoglobin, casein, plant albumins, such as crystalline edestine, etc.

Carbohydrates—Agar (δ -galactose), starch, gum arabic, cherry gum, tragacanth, vegetable glues, such as carrageen (Irish moss); Iceland moss, quince seed glue, etc. Soluble starch and dextrin form transition solutions between colloid and molecular disperse systems.

Soaps are colloidal in aqueous solutions and molecular disperse in dilute alcoholic solutions. **Rubber** is colloidal as a gel in benzene solution. **Cellulose** and its derivatives are colloidal as collodion; as viscose, which is an alkaline cellulose plus CS_2 in water; as filter paper in a solution of copper ammonium hydroxide and concentrated ZnCl_2 ; and as celluloid, which is a solid solution of camphor and cellulose derivatives. **Resins and resin soaps** are colloidal in mineral oils, etc. **Tannin** in water forms a colloid transition system.

Dyes—Typical colloid dyes in aqueous solution are: night blue, diamine blue, immedial blue, aniline blue, indigo, indulin, Congo red, benzopurpurin.

Transition systems are Congo rubin and azobblue.

Molecular disperse dyes in water are: methyl violet, acid fuchsine, safranine, methylene blue, brilliant green, etc. (See Expt. 48.)

Chlorophyll is colloidal in aqueous solution.

Colloidal indigo—Black particles. Colour of solution: blue black in reflected light; indigo blue in transmitted light. Indigo content, about 50 per cent.

Colloidal cholesterol—Amber yellow lamellæ. Colour of solution : milky in reflected light ; reddish in transmitted light. Cholesterol content, about 20 per cent.

Colloidal phenolphthalein—Brownish yellow, glistening lamellæ. Colour of solution : milky white in reflected light ; reddish in transmitted light. Phenolphthalein content, 50 per cent.

Colloidal tar—Dark brown glistening lamellæ. Colour of solution : sooty grey in reflected light ; reddish grey in transmitted light. Tar content, about 20 per cent.

DISPERSOIDS OF VARYING DEGREES OF DISPERSION

SULPHUR

1. Large sulphur crystals.
2. Roll sulphur, microcrystalline.
3. Sulphur flowers, microscopic sulphur globules.
4. Milk of sulphur is in a transitional state between coarsely disperse and colloidal sulphur. The aqueous suspension partially passes through an ordinary filter paper.
5. Aqueous colloidal sulphur, prepared according to Expt. 11, or the commercial preparations.
6. Dissolution of sulphur in paraffin oil, partially colloidal, according to J. Amann.
7. Molecularly disperse sulphur solution in CS_2 .

SODIUM CHLORIDE

1. Large rock salt crystals.
2. Crystalline common salt.
3. Ground table salt.

4. Sodium chloride gel. (Expt. 27.)
5. Sodium chloride-benzene sol. (Expt. 26.)
6. Molecularly dispersed aqueous sodium chloride solution.

Another colloid series consists of a variously dispersed gold ruby-glass in the three states described in a preceding paragraph: (1) Colourless to bright yellow when molecularly dispersed; (2) red to violet when colloidal; (3) blue and turbid with yellow brown colorations when coarsely dispersed.

Steel is a solid dispersoid, in which numerous structural constituents, such as the pure iron or ferrite, the iron carbide or troostite, the carbon or temper carbon, are in a state of colloidal dispersion. A coarsely dispersed as well as a molecularly dispersed state of the same constituents is found in other iron alloys. Colloidal carbon occurs besides the coarsely dispersed graphite as the molecularly dispersed hardening carbon. Specimens of iron of various grain sizes are likewise suitable for demonstration of a colloid series possessing different degrees of dispersion.

DISPERSOID SERIES ACCORDING TO THEIR PHYSICAL STATE

The following substances illustrate separate classes of dispersed systems, the dispersion medium being given first.

(a) **Liquid-solid**¹—Aqueous suspensions of quartz, animal charcoal, kaolin, etc., are coarsely dispersed. Colloidal gold, silver, etc., are suspensions. Aqueous sodium chloride solution is a molecularly dispersed system.²

(b) **Liquid-liquid**—Coarse emulsions of oil in water, such as commercial cod-liver oil emulsion, are coarsely dispersed:

¹ The dispersion medium is always given first.

² It should be pointed out that the concept of degree of aggregation no longer holds when the systems are molecularly dispersed.

Non-hydrated emulsoids. Colloidal emulsions of mineral oil in water, prepared in Expt. I, or colloidal sulphur, prepared in Expt. II.

Hydrated emulsoids. Aqueous solutions of gelatin, starch pastes, benzol-rubber solutions, collodion solutions, etc.

Solutions of alcohol in water are molecular disperse systems.¹

(c) **Liquid-gas**—Foams, prepared by shaking soaps or saponin solutions, albumins, etc., are coarsely disperse. Colloidal foams, as yet little investigated, are seen as critical phenomena during the liquefaction of gases when the opalescence in the fluid phase occurs. Carbon dioxide-water is a molecular disperse system.¹

(d) **Solid-solid**—Coagulated gold ruby-glass, metallic alloys, minerals such as granite, are coarsely disperse. Glass with colloidal colouring materials, steel, blue rock salt, smoky quartz and other coloured minerals, are colloids. Solid solutions, such as mixed crystals, alum, ammonium chloride and ferric chloride, etc., are molecular disperse systems.

(e) **Solid-liquid**—Minerals with microscopic liquid inclusions, such as milky quartz, crystals with occlusions of mother liquor or water, are coarsely disperse colloids. Solid systems with colloidal liquid occlusions are as yet unknown. The water contained within zeolites may be removed without affecting their form, probably because it is in a highly disperse state, existing both as colloidal drops and as a continuous phase. Crystals contain water of crystallization in molecular state.

(f) **Solid-gas**—Lava, meerschaum, pumice are coarsely disperse systems. Colloids of this nature have not yet been studied. Solutions of gases in solid substances, such as hydrogen in palladium, are molecular disperse systems.

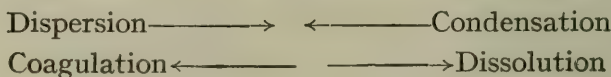
¹ See previous note.

(g) **Gas-solid**—Smoke, such as soot, produced by burning benzene in a spirit lamp, or ammonium chloride fumes, produced by pouring together a few drops of concentrated HCl and NH_4OH into an empty litre flask. The degree of dispersion of such systems is variable. The combustion products of a faintly luminous Bunsen flame are colloidal dispersed (H. Senftleben).

(h) **Gas-liquid**—Liquid fogs, such as water vapour, clouds, etc., or fuming HCl, are examples of typical cloud formations.

DISPERSE SYSTEMS

Coarse dispersion.	Colloidal.	Molecular dispersion.
Increasing degree of dispersion		
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">↓</div> <div style="text-align: center;">Particle sizes</div> <div style="text-align: center;">↓</div> </div> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;">↓</div> <div style="text-align: center;">to</div> <div style="text-align: center;">↓</div> </div> <div style="display: flex; justify-content: space-around; align-items: center; margin-top: 10px;"> <div style="text-align: center;">0.1μ</div> <div style="text-align: center;">$1\mu\mu$</div> </div>		
<p>Particles larger than 0.1μ, do not pass through filter paper, can be observed microscopically, not diffusible and non-dialysable.</p>	<p>pass through filter paper, are held by an ultrafilter, cannot be represented microscopically, may be recognized microscopically sometimes, not diffused and dialysable or only very slowly.</p>	<p>Particles smaller than $1\mu\mu$, pass through both ordinary filter paper and ultrafilter, cannot be recognized ultra-microscopically, diffuse and dialyse with remarkable rapidity.</p>



X

DISPERSOID ANALYSIS

A FREQUENT question is whether an unknown system has colloidal properties. The colloidal procedures outlined in this manual may be used to answer such questions. The following table gives a systematic scheme of analyses :

A. GENERAL DETERMINATION OF DEGREES OF DISPERSION

I. CHEMICAL ANALYSIS OF A HOMOGENEOUS SUBSTANCE

1. According to Expts. 77, 78, and 86, homogeneous appearing liquids (unless hylotropically convertible) possess definite boiling and freezing temperatures, normal molecular surface tensions, etc. } Normal liquids.

2. Physical mixtures of materials of similar analytical composition but of different physico-chemical properties, such as melting point, boiling point, density, solubility, etc. ; mixtures of isomers, polymers, allotropic substances and strongly associated liquids, etc. } Iso-dispersoids eventually isocolloids.

II. CHEMICAL ANALYSIS OF HETEROGENEOUS SUBSTANCES

Experiments of hylotropic transformations, such as vaporization, distillation, freezing, give two or more constituents of different chemical composition.

1. Substances appearing optically homogeneous, according to Expts. 77, 78 and 86. }
 Rapid diffusibility, according to Expt. 48. } Molecular
 Rapid dialysis, according to Expts. 52, 53, or } disperse
 54. } solutions.

2. Fluids appearing heterogeneous optically upon microscopic and ultramicroscopic examination.

(a) Macroscopic and microscopic heterogeneity; separation of components by ordinary filtration or by spontaneous settling, etc. Separation into two layers by moderate centrifuging; spontaneous separation (usually redispersable.) }
 Coarse }
 dispersions }
 (Suspensions }
 and }
 emulsions).

(b) Macroscopic, often turbid, opalescent (Expt. 92); positive Tyndall cone (Expts. 77 and 78), for differentiation of fluorescence). }
 Slow diffusion (Expt. 48); non-dialysable, } Colloidal
 according to Expts. 52, 53, or 54. } solutions.

B. SPECIAL COLLOID ANALYSIS

1. Viscosity not essentially greater than that of the dispersion medium; easily coagulated by electrolytes (Expts. 153-158); spontaneously ultrafiltered (Expt. 57). }
 Suspensoids.

2. Viscosity greater than that of the dispersing medium ; more difficult to coagulate by neutral salts ; decomposable by ultrafiltration (Expt. 57) ; resolvable ultramicroscopically. } Non-hydrated emulsoids.

3. Viscosity essentially greater than the dispersing medium, especially at small concentrations ; greater temperature coefficient of viscosity (Expt. 70). Difficult to coagulate by neutral salts (Expt. 162). Dispersion medium and disperse phase not completely separable by spontaneous ultrafiltration. Separate particles not recognizable ultramicroscopically, but only by Tyndall cone. } Hydrated emulsoids.

TABLE OF NORMAL SOLUTIONS

THE concentrations in grams per litre refer to the hydrated salts of the composition given. A molar solution of BaCl_2 contains, for example, 208.3 g. of anhydrous salt per litre. Since the usual commercial preparation has two mols of water of crystallization, the following table gives 244.3 g. dissolved in one litre of water, etc. The bracketed numbers denote that the molar or normal solution cannot be prepared on account of small solubility, which is given in column 3. The data of saturated concentrations are given for 15°C ., if not otherwise stated. The concentration data in column 3 also refer to the hydrated salts.

Substance.	Molar solution grams per litre.	Normal solution grams per litre.	Saturated solution grams per 100 grams of solution.
AgNO_3	169.9	169.9	64.9
AlCl_3	133.5	44.5	41.1
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	666.7	111.1	50.4
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	244.3	122.2	31.0
CaCl_2	111.0	53.5	41.0
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	219.1	109.6	80.9
CaSO_4	(136.1	68.1)	0.20
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	(172.2	86.1)	0.25
$\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$	256.5	128.3	92.6
CuCl_2	134.5	67.2	43.0
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.7	124.9	25.3
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	198.8	99.4	63.1
FeCl_3	162.2	54.1	46.4
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	270.3	90.1	77.3
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.0	139.0	35.4
Urea $[\text{CO}(\text{NH}_2)_2]$	60.1	—	42.0

Substance.	Molar solution grams per litre.	Normal solution grams per litre.	Saturated solution grams per 100 grams of solution.
Citric acid [H ₃ C ₆ H ₅ O ₇ .H ₂ O]	210.1	70.0	64.8
HgCl ₂	(271.5)	135.8)	6.54
Hg(CN) ₂	(252.6)	126.3)	7.4
KAl(SO ₄) ₂ .12H ₂ O	(474.5)	118.8)	8.75
KBr	119.0	119.0	38.9
KCN	65.1	65.1	—
KCNS	97.2	97.2	67.5
K ₂ CO ₃	138.2	69.1	52.5
KCl	74.6	74.6	24.4
KClO ₃	(122.6)	122.6)	5.79
K ₃ -citrate [K ₃ C ₆ H ₅ O ₇ .H ₂ O]	324.3	108.1	64.7 (30°)
K ₄ Fe(CN) ₆ .3H ₂ O	(422.6)	105.7	20.6
KI	166.0	166.0	58.4
KNO ₃	101.1	101.1	20.7
K ₂ SO ₄	(174.3)	87.1	9.25
Li ₂ SO ₄	109.9	55.0	25.7
MgCl ₂	95.2	47.6	35.1
MgCl ₂ .6H ₂ O	203.3	101.7	75.1
MgSO ₄ .7H ₂ O	246.5	123.2	51.0
NH ₄ CNS	76.1	76.1	60.7
NH ₄ Cl	53.5	53.5	26.0
(NH ₄) ₂ SO ₄	132.1	66.1	42.6
NaCl	58.5	58.5	26.4
Na-salicylate [NaC ₇ H ₅ O ₃]	160.0	160.0	52.0 (at 20°)
Na ₂ SO ₄	142.1	71.0	11.7
Na ₂ S ₂ O ₃ .5H ₂ O	248.0	124.0	62.0
Na ₂ SO ₄ .10H ₂ O	322.2	161.1	26.5
Oxalic acid [C ₂ H ₂ O ₄ .2H ₂ O]	(126.06)	63.03	10.2
Pb-acetate.3H ₂ O	379.3	189.7	ca. 30
PbCl ₂	(278.1)	139.1)	0.9
Pb(NO ₃) ₂	331.2	165.6	33.5
ZnSO ₄ .7H ₂ O	287.5	143.8	60.0

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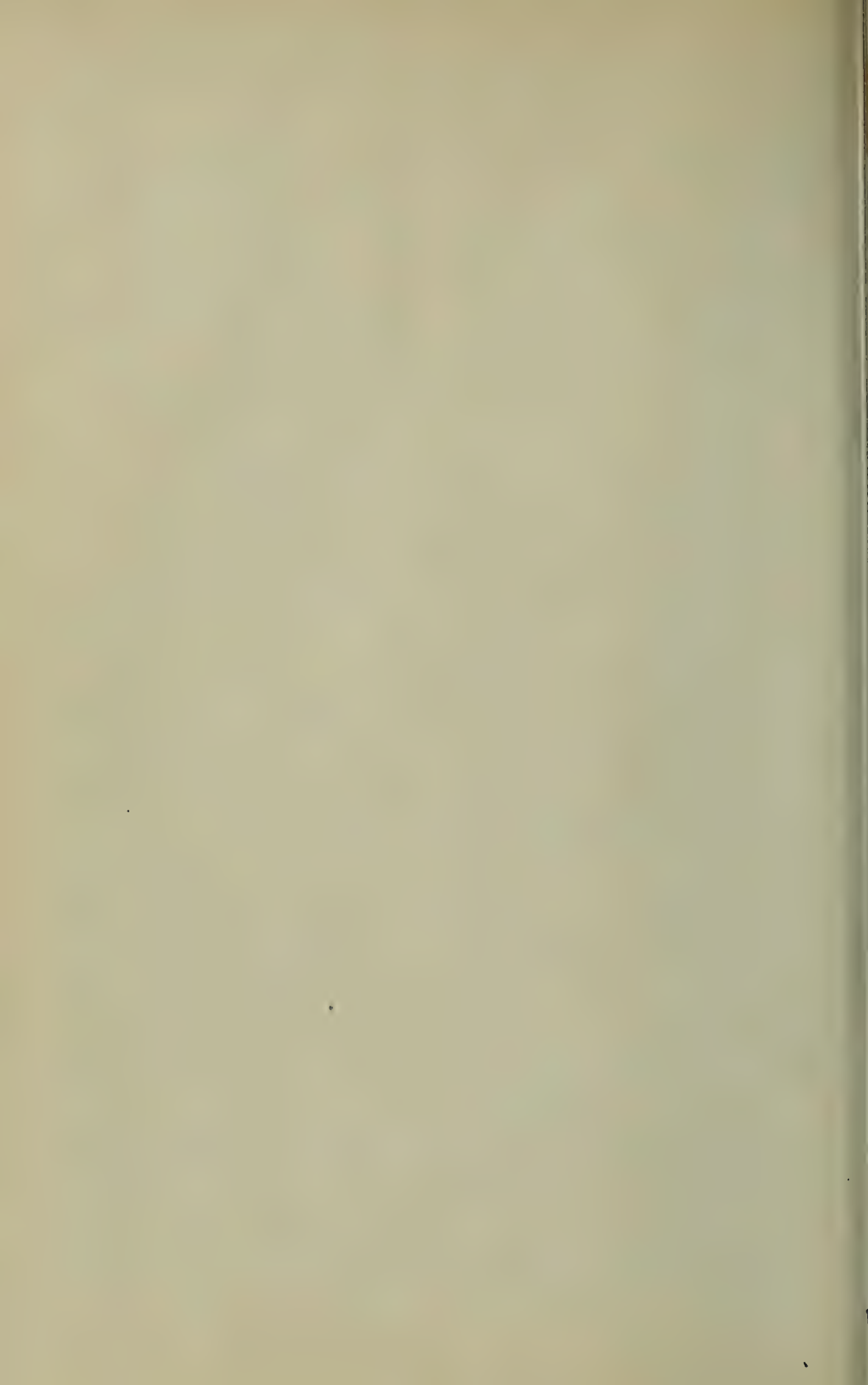
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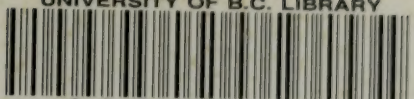
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